# CasaXPS Manual 2.3.15

# **CasaXPS Processing Software**

## Casa Software Ltd.

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# TOF SIMS

# The Nature of ToF Spectra

Time-of-Flight Mass Spectrometry (ToF MS) is based on the principle that ions created from a sample are accelerated into a flight tube using an electric extraction field resulting in each ion of a given charge acquiring a characteristic energy from a tight distribution of possible energies. Since the kinetic energy of the ions are nearly identical, the velocity attained by ions with differing mass must also differ, thus the time taken for an ion with a given charge to travel a given distance down the flight tube to the detector discriminates between ions of different mass. Specifically, the mass of an ion is proportional to the square of the time taken to travel a fixed distance. Thus, ToF MS works on the basis of a stop-watch; a start event occurs as the extraction voltage is pulsed, followed by a sequence of stop events representing the arrival of ions at the detector. To process a ToF mass spectrum from the raw timing data, a histogram is created from the set of time values, where the time events recorded during an experiment are counted into time-bins. The relationship between the time events and the mass of the ions responsible for the time events allows the time-bin histogram to be viewed using a mass scale.

CasaXPS displays the ToF intensities with respect to the time bin indices, even when a mass calibration is available. Converting a spectrum to mass binned intensities involves a mapping which cannot be reversed; explicit steps must be taken to perform the transformation between time and mass.

The following two plots are for the same data, both viewed in the time domain. The mass range in these two plots is identical.





The same spectrum plotted using a linear mass step size changes the perspective of the data as follows.



Spectra from ToF instruments traditionally appear as a single spectrum over a wide range of mass. The spectral display reflects the parallel nature of the technique in the sense that counts are allocated over the entire range of time bins for each pulse of the ion gun. This is in contrast to quadrupole or magnetic sector MS instruments where the signal is only recorded one mass bin at a time. Nevertheless, for high resolution ToF MS the majority of time bins, particularly at low mass, contain little information, therefore CasaXPS offers a means of converting ToF spectra from a single monolithic data set into a set of mass intervals representative of the useful information, is isolated into individual VAMAS blocks. Presenting a ToF spectrum as a set of many

VAMAS blocks favours the tools within CasaXPS providing the basis for data comparison and peak analysis via synthetic peak models.



The partitioning of the time bins into suitable mass ranges around the nominal masses requires a calibration for the mass scale.

# **ToF Mass Calibration**

The relationship between the mass *m* of an ion and the time taken for the ion of a given charge to travel a fixed distance is quadratic in the flight time *t*. For an ideal system, the time-to-mass relationship is:

 $m = [(t - t_0)/b]^2$ 

where  $t_0$  represents a time offset and *b* scales the time values appropriately. Since knowledge of these two parameters  $t_0$  and *b* is sufficient to describe the relationship between the mass and time-of-flight, given two mass/time pairs the calibration parameters can be determined from a pair of simultaneous equations. In reality, assigning the mass/time coordinates from the time-binned spectra is not exact and therefore the time-to-mass calibration must be computed in a least-squares sense using multiple mass/time pairs. Further, the choice of mass/time pairs must be carefully made to ensure accuracy of the calibration for both interpolated and extrapolated mass regions. Those mass regions falling within (interpolation) the set of mass/time pairs used to create the calibration will be more accurate with respect to the time-to-mass calibration than those outside (extrapolation) the interval containing the mass/time pairs included in the least squares fit. It is therefore important to calibrate a spectrum using peaks over as wide a mass range as possible and check that peaks, once calibrated, can be sequentially assigned to nominal masses. The following describes the tools in CasaXPS for calibrating a spectrum of time-bins with respect to mass and how to assess the success of this procedure.



Figure 2: An example of a poor mass calibration based on extrapolation.

When calibrating the mass scale, the primary objective is to assign each visible peak to a nominal mass. For some spectra and instruments, there may be perfectly good reasons why this objective may fail, but in general each peak in the data should be associated with a nominal mass; any mass defect from the nominal mass provides information about the atomic or molecular ion responsible for the peak. It is not necessary nor is it always possible to attribute each peak to a known ion, however, when properly calibrated, if the observable peaks deviate from the sequence of nominal masses then the accuracy of the calibration may be in doubt. The problem of calibrating the mass scale reduces to identifying a set of peaks sufficiently well distributed over the mass scale to provide plausible mass assignments for each and every

peak in the spectrum. Figure 1 is an example of a mass calibration in which the set of peaks displayed matches well with the computed mass positions; however the calibration is performed using only those peaks within the window in Figure 1 and a similar agreement, when using the same calibration, for the molecules shown in Figure 2 is not achieved. The poor mass calibration is remedied by simply including at least one of the peaks in Figure 2 as part of the calibration set. The concept of progressively adding calibration points to the set used to mass calibrate a spectrum is developed in following sections.



#### **Calibration Based on Nominal Masses**

Figure 3: Nominal mass calibration

The procedure for calibrating a spectrum can be summarised as follows: following an initial assignment based on at least two peaks, new peaks are progressively added to the set of mass/time pairs until the observed peaks are sequentially associated with nominal masses. The spectrum in Figure 3 is calibrated based on nominal masses and an iterative improvement procedure. This process can be performed manually using the Exact Mass property page (Figure 4), where peaks are associated with formulae using the mouse, or alternatively nominal masses are used in a sequence of steps involving repeatedly:

1. Finding the peaks using the Find Peaks button.

- Replacing the current calibration list by nominal masses and times determined from the regions obtained from the Find Peak operation. The Load Regions button transfers the required information from the current set of regions to the calibration list on the Exact Mass property page.
- 3. Recalibrate the mass scale by pressing the Calib C,t0 button.

Element Library			. 🗆 🖂
Element Table Periodic Table	Input File	Exact Mass	
Name	Mass	Time Bin	F
143	143 151	52119.4 53470.4	
152	152	53638	
15/	157 168	54469.1 56239.8	
170	170	56557.6	
171	171	56713.7 56992 5	
182	182	58417	-
183	183	58557.2	✓
		>	
40			
Add Formula 🗖 Define Tir	me 3PC	alib Calib (	C,10
Delete Entry Clear Mar	kers	Find Peal	ks
Delete All 📃 Zoom	Create	Load Regi	ons
		Create Pe	aks
Load Save	Move to L	.ib Ex M	Т

Figure 4: Exact Mass Calculator Property Page.

The Find Peaks button uses a threshold to identify peak structures in the data; then for each peak identified, a region is created on the spectrum using the name derived from the nominal mass determined from the region. The Load Regions button transfers those nominal mass names and computed positions to the calibration table on the Exact Mass property page for which the computed mass is within a tolerance of the nominal mass. The search for these acceptable mass/time pairs begins with the low masses, so the initial calibration should begin with small masses, but typically greater than 10 amu. With each repetition of these steps, the number of regions loaded into the calibration table should increase until, ideally, all the peaks found are included in the calibration table. At this point, the spectrum so calibrated should be surveyed to ensure the peaks, both minor and major, are associated with the nominal masses on the abscissa scale.



Figure 5: Raw time-binned spectrum.

Calibration using nominal mass values is not always appropriate, for example heavy molecular ions; however, for some spectra, calibration using exact masses is equally inappropriate. The data in Figure 1 is an example of a spectrum for which it is beneficial to use nominal masses rather than exact masses; the spectrum derives from a total ion list file containing image information and minor variations in acquisition conditions across the imaged surface cause small shifts in the underlying peaks summed to form the total ion spectrum. Peaks are neither high enough in mass resolution nor well enough defined in terms of position to use an exact mass position. The latter can be demonstrated using false colour images to extract spectra from different zones on the image.

#### An Example of Mass Calibration using Nominal Masses

Initially the spectrum is without a mass calibration as seen in Figure 5. The first step is to identify two peaks.



Figure 6: Two peaks are identified by creating quantification regions.

The regions defined on the spectrum in Figure 6 represent the initial pair of mass/time coordinates used to produce a rough calibration for the mass scale. The regions are created using the Regions property page on the Quantification Parameters dialog window. Each region calculates the timebin representative of the peak, while the mass corresponding to the computed time-bin is entered into the name field of the quantification region. In this case, the name fields are entered with the nominal masses 15 and 23, although these values could equally well have been entered using the formulae C+H\*3 and Na, respectively. Calibration based on these two regions is performed by pressing the Interest button. When the toolbar button is pressed, any spectra appearing in the Active Tile will be calibrated based on regions so defined on the displayed spectra.



Figure 7: Spectrum after initial mass calibration.

While the calibration in Figure 7 looks reasonable for masses close to the calibration points, the high mass peaks are poorly calibrated. The largest peak in Figure 8 differs by about 18 amu from the mass calibration shown in Figure 3.



Figure 8: Poor mass calibration for high mass peaks. Same peaks as those displayed using the inset tile in Figure 3.

While the initial mass calibration based to only two low mass peaks is clearly a problem at higher masses, the accuracy is sufficient to begin the iterative process of build a fuller set of mass calibration points.

	Element Lil	brary			
E	lement Table	Periodic Table	Input File	Exact Mass	
	Name		Mass	Time Bin	Rel./
	15		15	18991.4	1
	18		18	20488.5	1
	23		23	22/03.9	-
	27		27	24391.8	
	28		28	24777.2	i
	29		29	25161.1	1
	30		30	25529.3	1
	31		31	25902.1	1
	<				>
	C+H*3				
	Add Formula	🗌 🗆 Define Ti	me 3P C	alib Cali	6 C,10
	Delete Entry	Clear Ma	rkers	Find Pe	eaks
	Delete All	C Zoom	Create	Load Re	gions
				Create F	Peaks
	Load	Save	Move to L	.ib Ex I	ЧΤ

Figure 9: Exact Mass property page.



Figure 10: Result of Find Peaks with a threshold of 20.

Given the initial mass calibration based on the peaks labelled 15 and 23, the Find Peaks button on the Exact Mass property page shown in Figure 9 can be used to assign nominal masses to all peaks characterized by a threshold value. On pressing the Find Peaks button, a dialog window appears in which a threshold value can be entered. In the case of the results shown in Figure 10 the threshold value was set to 20. Once a new set of regions are created using the Find Peaks button, the Load Regions button is pressed, the consequence of which is the mass calibration table on the Exact Mass property page is loaded with the set of calibration points determined from the regions currently defined on the spectrum, subject to the condition that the mass determined from the time bin for each region is within a tolerance of the nominal mass entered into the name field of the region. Following the initial mass calibration and application of the Find Peaks button, the set of regions generated by the Find Peaks button in Figure 10 are limited by the Load Regions button to those displayed in Figure 9. That is, all regions above nominal mass 31 were sufficiently different from the nominal mass to be rejected. The deviation of the computed mass for peaks above 31 amu from the nominal mass is a measure of the error in the original mass calibration. Given the new set of calibration points, the Calib button on the Exact Mass property page can be pressed resulting in an improved mass calibration. Repeating the Find Peaks operation followed by reloading the regions into the calibration table reveals that peaks up to 53 amu are now included in the calibration table. A third iteration of these steps produced a calibration table including peaks up to 228 amu, while a forth iteration extends the calibration table up to 561 amu, exhausting the set of peaks found using the Find Peaks button. The mass calibration based on nominal masses is now complete. All that remains is to verify the mass calibration by stepping through the spectral peaks to confirm the presence of peaks at each amu and that known peaks







The procedure is not without flaw, so verification is necessary, but can provide a means of improving an initial calibration with minimal effort. For high resolution ToF spectra, the use of nominal masses will lead to a rough mass scale which requires refinement using resolved peaks and exact mass formulae (Figure 11).

NB: The peak marker in Figure 11 for elemental Si is positioned to the lefthand side of the peak. When a ToF spectrum is calibrated using the option on the toolbar, the position of peaks with respect to time are determined from the regions. While the peak maximum may appear to be a good choice for the peak position, the asymmetry typically observed in ToF peaks and the variety of peak shapes over a spectrum suggest, in general, the peak maximum is less well defined than the leading edge of a peak. For this reason, the position of the peak used for the calibration procedure is taken to be the lower full width half maximum. Hence the peak markers will align with the leading edge of the peaks rather than the peak maxima. Note that the calibration option on the Exact Mass property page offers the choice of peak position to the user without limitation.

## **Recalibration of Mass Scale for ToF Spectra**

Occasionally ToF Spectra are supplied as mass binned data. While data in mass bins is convenient for those without the ability to handle the relatively large time binned spectra, the possibility exists that the mass calibration used to mass-bin the spectra may not be accurate enough for the application in question. For high resolution mass spectra, a small error in the original time-to-mass calibration may lead to the type of uncertainty illustrated in Figure 12, where the peak maximum falls between the two most likely assignments for the measured data. A recalibration of the mass bins is therefore required.



Figure 12: An example of a mass-binned spectrum where the original mass calibration is not sufficiently accurate for the resolution of the peak shown.

The recalibration of mass-binned data differs from a time-to-mass calibration of time-binned data in that the act of reallocating the counts to mass-bins from the original time-binned data (performed during the creation of the mass spectrum), results in the loss of information. Namely, two or more time-bins may map into the same mass-bin, therefore it is impossible to take a mass-bin and repopulate the time-bins with the same distribution found in the original data set. The consequence of there being a fundamental difference between these two operations is that, when recalibrating a massbinned spectrum, the functional form used to assign the data bins to mass values must involve a general three parameter quadratic function rather than the stiffer model used to calibrate time-bins to mass-bins. The two parameter calibration function recommended for time-to-mass calibration is too specific to the counting mechanism used to acquire the ToF MS data. The extra flexibility offered by the three parameter quadratic is needed to model the errors in the original time-to-mass calibration; the stiffer two-parameter quadratic model used for time-to-mass calibration is dictated by and appropriate to the physics of the ToF instrument.

While CasaXPS allows time-to-mass calibration using both the recommended two-parameter quadratic model and the general three-parameter quadratic function, the same warning about the three-parameter functional form is equally applicable to both situations. That is, the flexibility offered by the general quadratic function allows non-physical solutions for the mass assignment of peaks. It is possible to create a mass calibration when using the three-parameter quadratic for which known peaks are apparently correctly assigned to masses, yet other peaks in the spectrum are incorrectly assigned. Extrapolation based on the three parameter model should be viewed with suspicion. Ideally, ToF MS data should be provided in the time domain, nevertheless situations do occur where mass-binned data must be managed and therefore CasaXPS provides a mean of recalibrating the mass-binned data. Figure 13 shows the same data seen in Figure 12 following the recalibration procedure described below.



Figure 13: The same mass spectrum after recalibration.

#### **Recalibration Steps**

- 1. Cancel the Mass calibrated status of the spectra: overlay the massbinned spectra in the Active Tile and press the 🕅 toolbar button on the SIMS toolbar. The label for the abscissa will return to "Time Bin", which indicates the data is in a state where a new calibration can be created. Note, the abscissa values will be bin indices, not true timebins, but nevertheless it is necessary to the calibration procedure that the abscissa label is assigned the string "Time Bin".
- Using the Exact Mass Calculator, a new calibration set defining the relationship between the peaks and the mass assignment must be established. The procedure is identical to creating a time-to-mass calibration described elsewhere.
- 3. Perform the recalibration using the Button on the Exact Mass Calculator property page of the Element Library dialog window.



Figure 14: A mass-binned peak illustrating the peak deformations due to the re-binning algorithm used to create the mass spectrum.

An alternative procedure is to create quantification regions and apply the recalibration using the *Internation* button. While possible, this approach suffers from the information lost during the time-to-mass conversion procedure, that is, the mass-bins for higher mass values tend to be poorly defined compared to the original time data (Figure 14). The algorithms for identifying a peak position and therefore determining the calibration points

assumes the data obeys Passion statistics, but otherwise varies smoothly; it is clear from Figure 14 that the mass-binned data contains anomalous values.

# **Peak Fitting ToF SIMS Data**

The features in CasaXPS typically used to model XPS data envelopes can also be used to analyst overlapping peaks in high resolution ToF SIMS spectra. The principal difference between ToF SIMS and XPS is that asymmetry in ToF SIMS peaks is, in general, in the opposite direction to that found for XPS peaks. As a result, not all line-shapes in CasaXPS are appropriate for ToF SIMS peaks, however the more recently introduced asymmetric line-shapes of LA and LF provide a means of creating line-shapes appropriate for the range of ToF SIMS peaks observed in practice.

The data in Figure 15 illustrates the similarities between XPS and ToF SIMS, where the mass peaks associates with a nominal mass of 42 are very typical of polymer XPS spectra such as PMMA or PET. The problems of understanding the data are also similar in that both the position and the intensity of the underlying peaks are of importance when identifying the molecular ions responsible for the measured data.



Figure 15: Example of ToF SIMS peak structure.

The procedure for adding synthetic components to the data involves first adding a quantification region to the data with background type set of "Zero" before adding synthetic line-shapes. Creating and adjusting regions and components is performed on the Quantification Parameters dialog window available from the Quantify option on the Options menu or the button on the top toolbar of CasaXPS. Regions and components are managed using the tables found on the **Regions** and **Components** property pages of the Quantification Parameters dialog window shown in Figure 16.

The peaks shown in Figure 15 are defined using the parameters displayed in the table on the Components property page illustrated in Figure 16. The line-shape parameter in this example is defined using the **LA** functional form, where the parameters provide a degree of asymmetry to the right of the peak maximum. The meaning of these parameters is described below.

	Quantification Parameters						
B	Regions Components Data Editor Report Spec. RPT Report						
	42 [RMS = 653.708; D. of F. = 77] [Eff. RSF = 0.998182] [Eff. M						
	A	В	С	D			
	42 a	42 b	42 c	42 d			
	1	1	1	R.S.F. =			
	LA(4,2.7,0)	LA(4,2.7,0)	LA(4,2.7,0)	LA(4,2.7)			
	6.8	3.8	2.5	Area = 22			
	0.0,10000	0.0 , 10000	0.0 , 10000	Area Constr. =			
	0.00694442	0.00576878	0.00576878	fwhm = 0.005			
	0.001639 ,	C*1	1e-005,1	fwhm Constr.			
	42.0114	42.043	42.0354	42.0474			
	41.9988 , 4	41.9988 , 4	41.9988 , 4	Pos. Constr. =			
	NoTag	NoTag	NoTag	NoTag			
	0	2	3	1			
	-0.2187	-0.2187	-0.2187	-0.2187			
	19.12	10.72	7.01	63.15			
	<			>			
	Create	💌 Marq	uardt	Paste			
-		O Simple	ex				
	Copy All	Carrier and the second		Paste Replace			
	Сору Ан	Fit Components					
	Сору	🔽 Use R	Monte Carlo				
	Cut	Fit 9	Copy and Fit				
	STO RCL	RST Fit	Step BG	Copy Names			

Figure 16: Quantification Dialog Window.

#### Line-shapes Suitable for ToF SIMS Spectra

The success of a peak fit is dependent on an appropriate choice for the lineshape parameter. As stated above, the **LA** and **LF** line-shapes offer sufficient flexibility for most ToF SIMS peak shapes.

The Lorentzian line-shape with FWHM F and position M is given by

$$L(x:f,e) = \frac{1}{1+4\left(\frac{x-e}{f}\right)^2}$$
 (1)

The functional form is symmetrical about x = M. In order to retain the characteristics of the Lorentzian line-shape and yet also introduce asymmetry, the **LA** line-shape is defined in two halves as

$$LA(x;\alpha,\beta,f,e) = \begin{cases} [L(x;f,e)]^{\alpha} & x \le e\\ [L(x;f,e)]^{\beta} & x > e \end{cases}$$
(2)

 $LA(\alpha,\beta,m)$ : Equation (2) defines the first two parameters used in the lineshape  $LA(\alpha,\beta,m)$  shown in Figure 16. The third parameter **m** is used to control the width of a Gaussian convolution applied to the functional form defined by Equation (2). As a consequence of the definition for the LA lineshape, an asymmetry line-shape is established by specifying **a** not equal to **β**. Further, is **a** is greater than **β** then the resulting peak will be asymmetric with an extended tail to the right of the peak maximum. Adjusting the Gaussian convolution parameter causes the extent of the asymmetric tail to reduce and also shifts the peak maximum towards the extended tail.

**LF**( $\alpha$ ,  $\beta$ , w, m): Identical to the LA line-shape with the exception that the specified values of  $\alpha$  and  $\beta$  are force to increase to a constant value via a smooth function determined by the width parameter w. The w parameter is used to restrict the extent of the tail.



Figure 17: Asymmetric Mass Peak fitted using a single LA line-shape.

By way of example, the elemental sodium mass peak shown in Figure 17 exhibits significant asymmetry to the right of the peak maximum, which can be modelled using the LA line-shape. Note that the line-shape included in the annotation of the peak in Figure 17 is achieved by setting the first parameter to a value greater than unity, thus compressing the tail to the left compared

to the tail to the right. Further, the Lorentzian tail to the right of the peak maximum is adjusted by convoluting the functional shape with a Gaussian of characteristic width described by a value of 250 for the *m* parameter in the LA definition. The degree of asymmetry is determine by the relative size of the first parameter compared to the second, that is  $\alpha > \beta$ .





The line-shape used in Figure 17 should be compared with the line-shape in Figure 18 corresponding to a similar sodium peak measured using the same lonToF instrument but using a different ion gun. The peak in Figure 18 rises more quickly than the peak in Figure 17, therefore the  $\alpha$ -parameter is now much larger than the  $\beta$ -parameter, which is also set to a value greater than unity. The larger the values for these two parameters the steeper the edge of the peak appears. Also note in Figure 18 that the Gaussian convolution is much narrower than that used in Figure 17. Possible values for the Gaussian parameter are between 0 and 499;  $\mathbf{m} = 0$  corresponds to no convolution being performed.

# **Peak Identification and Reduction**

High resolution ToF spectra typically consist of numerous peaks, however for some analyses only a small number of correlated peaks are significant for distinguishing between samples. That is, a peak at one mass is only characteristic of a particular compound when also accompanied by peaks at a set of very specific masses. Given the plethora of peaks typically present in ToF MS data, a means of grouping and displaying only significant peaks is required. To visualise the spectrum with respect to only significant peaks, a ToF spectrum can be organised in CasaXPS 2.3.15 such that the Element Library property page simplifies the mechanism by which these significant peaks can be displayed for visual inspection. In addition to the element marks, a spectrum can be broken into an array of VAMAS blocks representing the peak information associated with the nominal masses and the element library used to display appropriate subsets of these VAMAS blocks for interpretation.

The procedure for splitting a ToF spectrum into a set of mass calibrated VAMAS blocks can be performed using the toolbar button indicated in Figure 19. As an alternative approach, for data files for which a mass calibration is available to CasaXPS at the time of conversion the division of the data into mass calibrated VAMAS blocks can be performed at the time the data are converted. Either route to the mass calibrated VAMAS blocks requires a mass calibration for the data.



Figure 19: ToF Spectrum with data in time domain.

The data in Figure 19 are converted to a mass calibrated set of VAMAS blocks

by pressing the toolbar button with hint **Split into Unit Mass Spectra**. The result of converting the data in Figure 19 is shown in Figure 20, where the right-hand pane displays the set of VAMAS blocks derived from the single VAMAS block in Figure 19.

The display in Figure 20 is achieved by overlaying the full set of VAMAS blocks from the right-hand pane in the active tile. An inset tile is used to display a specific VAMAS block, namely the VAMAS block corresponding to a nominal mass of 42. Note that since the individual VAMAS blocks are mass calibrated, the overlay appears in the form of a mass calibrated spectrum.



Figure 20: ToF Spectrum after conversion to mass calibrated VAMAS blocks.

The discussion that follows relates to data prepared in the format shown in Figure 20. Presenting the spectrum as a set of VAMAS block provides the basis for the tools within CasaXPS. Before describing these tools, the method for converting data files directly to mass calibrated sets of VAMAS blocks will be addressed. Version 2.3.15 of CasaXPS only offers data conversion to the multiple VAMAS block format for ASCII files formatted using the convention adopted by the IonToF data system.

# IonToF Peak Identification

IonToF spectra are exported in ASCII files in the format shown in Figure 21. The follow describes the options in CasaXPS for importing these data in formats suitable for compiling peak lists.

📕 1.txt -	Notepa	ad		
<u>F</u> ile <u>E</u> dit	F <u>o</u> rmat	<u>V</u> iew	<u>H</u> elp	
channel	mass	i	ntensity	~
Compres	sion H	acto	r = 1	-
16720	1.000	024	0	
16721	1.000	138	0	
16722	1.000	253	0	
16723	1.000	368	0	
16724	1.000	483	0	
16725	1.000	598	0	
16726	1.000	713	0	
16727	1.000	828	0	
16728	1.000	943	0	
16729	1.001	058	0	
16730	1.001	173	0	~
<				≥:

Figure 21:IonToF ASCII format.

The SIMS toolbar in CasaXPS offers two toolbar buttons for controlling the import of data in the format shown in Figure 21. These toolbar buttons are indicated in Figure 22.



#### Figure 22: SIMS Toolbar buttons

The traditional method for working with ToF data is based on a single data block approach, however the tools for peak identification now added to CasaXPS are organized on a partitioning of the data into numerous data blocks based on the nominal mass for each group of peaks. The objective is to analyze a directory of spectra and determine a set of mass peaks and intensities for each spectrum in the directory.

### Converting IonToF Spectra 🖃

Convert and Merge Directory of Spectra		? 🔀
Look in: 🗁 for Neal 1	- + 🗈	<b>r≣</b> *
<ul> <li>1.txt</li> <li>2.txt</li> <li>3.txt</li> <li>4.txt</li> </ul>		
File <u>n</u> ame:		<u>O</u> pen
Files of type: All Files (*.*)	•	Cancel

Figure 23: ASCII txt files exported from the IonToF software.

A data directory initially contains a set of spectra exported from the IonToF software as ASCII txt files. Figure 23 illustrates such a directory which is displayed using the File Dialog window offered by the *toolbar* button. The conversion of these data may be performed using several filter strings as follows:

- 1. ".ion"
- 2. ".amu"
- 3. ".sum".

To initiate a conversion sequence, a name followed by one of the above strings must be entered into the File name text-field on the File Dialog in Figure 23. For example, to convert and merge the set of txt files in a format suitable for peak identification, the File name text-field should be entered with the string "datafile.amu". The base-name is arbitrary, however the extension ".amu" instructs the set of txt files to be converted to VAMAS format (a new VAMAS file will appear in the directory for each txt file processed) then these converted files are merged into a single experiment frame in CasaXPS. Note that these data are large; therefore the process is both time consuming and requires plenty of PC memory!

The different filter strings determine the nature of the data files generated from the IonToF ASCII files. The individual VAMAS files generated from the ASCII files are identical for both the ".amu" and ".sum" filters; the final outcome differs however, where the ".amu" filter causes the merger of the spectra into a single experiment frame as separate spectra equivalent to the original ASCII data, while the ".sum" filter results in the total counts from the set of spectra in the ASCII files forming the equivalent of a single mass spectrum. In both cases, the mass spectrum from each of the IonToF files is partitioned into VAMAS blocks corresponding to data in the vicinity of the nominal mass values. Figure 24 shows the result of using the ".sum" filter on the data directory depicted in Figure 23. Both display tiles in Figure 24 display an overlay of *all* the data blocks in the right-hand pane of the experiment frame and the inset tile shows the data from the three highlight blocks containing intensities for nominal masses 41, 42 and 43 amu.



Figure 24: Example of a total counts spectrum formed from the four ASCII files shown in Figure 23.

The conversion filter ".ion" when applied to a directory merges the data into a single experiment frame containing one spectrum per original ASCII file, but maintains the data for each spectrum as a single block. While the format adopted is more traditional for mass spectra, the peak identification option uses peak-fitting and therefore the format shown in Figure 24 is more suited to the algorithms involved. The single block of data provided by the ".ion" is for visual inspection of the full data set and should not be used when peak identification is employed.

# **Directory Profiling**

The objective addressed by the features described here, is to identify and quantify in terms of mass assignments and intensities the set of peaks characteristic of a sample. The peak structures within a ToF spectrum are illustrated in Figure 25, where it can be seen that at least five overlapping peaks to varying degrees are responsible for the data envelope. Peak intensity and peak position are determined for these types of peak structures using optimized peak modelling. The very fact that peak modelling is required highlights the difficulty of automatically identifying all the peaks for a given data envelope. For a directory of similar spectra, automatically identifying mass peaks from data such as that in Figure 25 is fraught with dangers and therefore the strategy in CasaXPS for processing directories of similar spectra is one of aiding the construction of a template spectrum, for which peak models are prepared to be exhaustive with respect to the data under analysis, then the automatic application of the template models to a

directory of spectra forms the basis for extracting the quantitative information for each spectrum in the directory.



Figure 25: Mass peak structure from a ToF spectrum.

The creation of peak models for each significant mass peak in a file such as the one shown in Figure 24 is central to the profiling options in CasaXPS. About 500 data blocks corresponding to the nominal masses potentially require the construction of regions and synthetic peaks. The success of the template approach relies on the peak models adequately describing the peaks with appropriate constraints in terms of relative positions and FWHM to permit the peak intensities to be calculated from the fitted model. To assist this initial step, an option on the Exact Mass Calculator property page of the Element Library dialog window offers a means of creating peak models based on a threshold limit.

The **Create Peaks** button on the Exact Mass Calculator property page (Figure 26) uses the threshold value to limit the number of peaks created for a given data block.

🗖 Element Library
Element Table   Periodic Table   Input File Exact Mass
Name Mass Time Bin Rel.J
MS Peak Threshold
ОК
Cancel
Threshold Counts 700
Noise Filter Width 5
Noise Filter Depth 6
Delete Entry Clear Markers Find Peaks
Delete All Zoom Create Load Regions
Create Peaks
Load Save Move to Lib Ex M T

Figure 26: Exact Mass Calculator Property page.

The peak creation mechanism uses the threshold value entered on the **MS Peak Threshold** dialog window to create a region and synthetic peaks for each data block overlaid in the active tile. The smaller the threshold values, the smaller the peaks will be that are included in the peak search. Since the significance of mass peaks may not depend entirely on peak intensity, it is worth noting that different threshold values may be appropriate for different ranges in the mass scale. It is therefore unlikely that a single application of the **Create Peaks** button will generate all the appropriate peaks, however, by the user selectively overlaying data blocks and choosing different thresholds, peaks can be created on large numbers of data blocks while still retaining the discretion of the operator. Ultimately, the success or failure of the profiling step will depend on the way these peak models are constructed and time spent in getting these models right will be recovered by the accuracy and automatic application of these models to larger data directories.

## Profile Directory Toolbar Option

The options for profiling a directory of IonToF spectra are as follows:

- 1. ".amu"
- 2. ".fit"
- 3. ".vfc"

These conversion filters are used to control the nature of the directory profile. On providing a base name followed by one of these filter strings, the directory located by the File Dialog window invoked by the toolbar button

is scanned for the appropriate file types and, on accepting the Continue prompt via the resulting message dialog, the set of files are one-by-one processed to produce several text file reports and a VAMAS file containing the profile information from the directory.

The two profile filters ".amu" and ".fit" both require a template spectrum to be loaded and displayed in the active tile. In the case of the ".amu" profile filter, the ASCII .txt IonToF files are converted to VAMAS files before applying the template information to these newly converted data, which are also saved in the processed state as .vms files. On completion, several text files provide the results of the profile, one offering the context information for the numerical tabulations located in the other files. In addition, the profile information is presented in VAMAS format within the current CasaXPS session. The second profile filter ".fit" performs the same sequence of steps as the ".amu" with the exception that the files processed from the directory are the ".vms" files. This removes the conversion step from the operation and is appropriate if, for example, the data directory has been previously processed using the ".sum" conversion filter described above. The ".sum" conversion filter generates a single spectrum from a set of files in a directory and also, as part of the process, converts the ASCII files to VAMAS format. The total counts spectrum created from the ".sum" operation may appear in the same directory as the converted files, but provided the filename retains the ".sum" sub-string, the total spectrum will not appear in the final profile results generated from applying the template file to the set of .vms files in the current directory.

An alternative way to profile a directory of .vms files is to apply the ".vfc" profile filter. In this case, no fitting is performed, but rather the existing peak fits within the set of VAMAS files is used to construct the profile information. The ".vfc" profile filter allows the individual files to be inspected and any anomalies rectified on a file-by-file basis before creating the profile information. It is important that the same set of VAMAS blocks and number of synthetic peaks are used on each of the data blocks, however profiling the directory without automatic peak fitting allows user-intervention to override poor fitting scenarios.

# Working with ToF Spectra in CasaXPS

# Time to Mass Calibration Procedures

A raw ToF spectrum is recorded in the time domain. Mass calibration of a ToF spectrum is performed in CasaXPS by identifying a set of peaks in the data with specific masses; then, by using these pairs of mass/time values a quadratic relationship between the time and mass scales is created. A linear least squares procedure determines the two constants within the quadratic expression and therefore two or more mass/time pairs must be supplied to perform the calibration procedure. The accuracy of the mass-to-time calibration is dependent of the precision of the mass/time pairs used in the least squares calculation; the more pairs used to compute the least squares solution, the more tolerant the calibration will be to errors in the mass/time specification.

CasaXPS offers two methods for calibrating ToF MS data:

- 1. Peaks and corresponding masses specified using quantification regions.
- 2. Mouse identification of the peaks coupled with an exact mass calculator located on the Element Library dialog window.

# Mass Calibration using Regions and Propagation of Regions between Spectra

The Quantification Parameters Dialog window provides a means of defining time intervals, within which systematic positions are defined (computed from a peak bounded by an interval) and linked to masses via an exact mass formula entered into the Name field for the regions.



Figure 27: Quantification Parameters Dialog Window shown three regions defined for the purpose of calibrating the time scale to mass.

The spectrum in Figure 27 is an example of ToF SIMS data where three quantification regions are defined suitable for calibrating the time scale to mass. The mass associated with each region is entered into the Name field and may be a numerical value exemplified by the region headed column **B** or a string corresponding to any exact mass formula equivalent to expressions use on the Exact Mass property page of the Element Library dialog window.



For example, the mass of a peak might be defined using the expression C+H\*3, which when evaluated would result in a mass of 15.0235 Daltons.

# Mass Calibration

One or more time domain spectra can be prepared with calibration regions as described above and overlaid in the active tile in the left-hand pane of the experiment frame. On pressing the *stoolbar* button, each spectrum in the active tile is calibrated using the peaks within the regions. Since multiple spectra can be mass calibrated using a single invocation of the toolbar button, the use of this procedure is supported by the propagation of the calibration regions to similar spectra, thus avoiding the need to manually create regions for each spectrum requiring a mass calibration.

#### **Propagation of Calibration Regions**

The procedure to propagate the calibration regions from the spectrum as defined in Figure 27 to two other similar spectra is as follows:

1. Select the VAMAS blocks in each of the two experiment frames containing the spectra requiring the calibration regions.



The CasaXPS window is arranged in a tiled format using the Tile option from the Window menu at the top of the CasaXPS main window. The arrangement of the experiment frames allows the selection to be made by left-clicking the first VAMAS block in the experiment frame to the bottom-left and then holding the Control-Key down and left-clicking the VAMAS block in the bottom-right experiment frame 2. The Browser Operations dialog window is invoked by right-clicking the mouse with the cursor over the left-hand pane of the top-most experiment frame. The objective is to right-click over the display tile in which the spectrum containing the calibration regions is displayed.

rowser Operation	5	
Propagate Regions	Processing     Annotation	OK Cancel
Components	Error Bars	
Match Species/Tra	nsition	
None	Regions C Comps C Combined	
Source: Wide	File Name	
Source: Wide Selected Block Id. Wide	File Name ed1 11 4 4 brun1-spectrum0_spc_calibrated.vms : c:\	documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-1t-4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-1t-4brun1-spectrum2_spc_calibrated.vms : c:\	documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-1t-4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-1t-4brun1-spectrum2_spc_calibrated.vms : c:\	documents and documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-1t-4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-1t-4brun1-spectrum2_spc_calibrated.vms : c:\	documents and documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-11:4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-11:4brun1-spectrum2_spc_calibrated.vms : c:\	documents and documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-1t-4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-1t-4brun1-spectrum2_spc_calibrated.vms : c:\	documents and documents and
Source: Wide Selected Block Id. Wide Wide	File Name ed11-1t-4brun1-spectrum0_spc_calibrated.vms : c:\ ed11-1t-4brun1-spectrum2_spc_calibrated.vms : c:\	documents and documents and

3. To propagate regions to the two selected VAMAS blocks, which are listed on the Browser Operations dialog window, tick the radio button in the Propagate section of the dialog window and press the OK button. Region labels are now visible on the spectra.



The data in each of the three experiment frames are calibrated by switching focus between the experiment frames and each time pressing the toolbar

button. Control-TAB moves the focus between the experiment frames within CasaXPS.



The time to mass calibration for the time domain data may be seen labelling the x-axis using a quadratic mass scale.



#### Mass Calibration using the Exact Mass Calculator Property Page:

The procedure for calibrating a spectrum involves creating a set of mass/time-bin pairs within the scrolled-list on the Exact Mass property page on the Element Library dialog window.

The example below illustrates how the columns in the scrolled-list headed Mass and Time store the information relating these two parameters. Before an assignment for a given entry has been made, the value in the Time column is set to -1. The mass for an entry in the table is computed from the chemical formula entered into the name column.

Element Library			
Element Table   Periodic Table	Input File E	xact Mass	Ì
Name C	Mass 12	Time Bin 65959.8	F
C+H*3 Na	15.0235 22.9898	-1 -1	=
L <sup>1</sup> U <sup>2</sup> 2+H <sup>3</sup> Si	26.9815 27.0235 27.9769	95784 -1 110005	
C + N + H <sup>*</sup> 2 C <sup>*</sup> 2 + H <sup>*</sup> 4	28.0187 28.0313	-1 110104	
C*2 + H*6 C*2 + H*7	30.0469 31.0547	-1 -1	<u>.</u>
AI		l	_
Add Formula	me 3P Calil	b Calib	5 C,10
Delete Entry Clear Mar	kers	Find Pe	aks
Delete All 📃 Zoom	Create	Load Re	gions
		Create P	'eaks
Load Save	Move to Lib	Ex N	4 T

To add an entry to the calibration table:

- Type a chemical formula into the text-field below the scrolled list and press the Add Formula button or press the return key on the keyboard. The formula for an ion may be entered using the chemical symbols used to on the Periodic Table property page of the Element Library dialog window.
- Select the name in the scrolled-list. To select a name field, place the cursor over the text within the Name column and left-click the mouse. The name entry will appear highlighted when successfully selected.
- 3. Zoom into the known peak in the spectrum displayed in the active tile. It is important to perform the zoom operation before step 4 is taken.
- 4. Tick the tick-box labelled "Define Time".
- 5. Using the mouse cursor, click on the known peak at a location representative of the mass already defined by the selected entry in the scrolled list. The value in the Time column is updated and the Define Time tick-box is cleared.

At least two entries must be specified in the scrolled-list before pressing the Calib C,t0 button on the Exact Mass property page. The more entries assigned mass/time pairs, the better the mass to time calibration will be computed in the least squares sense.

Once a calibration table has been prepared, a file containing the calibration points can be saved to a separate text file from the data.

Element Library				X		
Element Table   Periodic Table	Input File	Exact Mass				
Name C C+H*3	Mass 12 15.0235	Time Bin 65959.8 -1	F			
Save Library File					?	×
Save in: 🛅 Kore		•	🗢 🔁	<b>r</b> 🗄	H.	
atest152						
File <u>n</u> ame: <u>ExactMass_calibra</u>	ationfile.lib				<u>S</u> ave	
Save as type: Lib. Files (*.lib)			•	0	Cancel	
Load Save	Move to L	.ib Ex	МΤ			

These files can be reloaded at a later time to provide an initial calibration for other data or for making adjustments to the calibration of the original spectrum used to create the calibration file. Note, while the Save button on the Exact Mass property page saves the current calibration table, the Load button will merge a saved file with the current set of entries on the scrolledlist. To return the table to the entries within a file, it is first necessary to press the Delete All button. The Delete All button removes the current entries in the scrolled-list, while the Delete Entry button removes the currently selected entry.

If an assignment is incorrect, the individual entry must be deleted from the table. The name field for the deleted entry is entered into the text field below the scrolled list; therefore a selected entry can be deleted then reinstated by immediately pressing the Add Formula button. The Time field will return to a value of -1 and therefore be ignored during any subsequent calibration operation.

#### The Element Library from a ToF Perspective

The element library in CasaXPS is an ASCII file. On startup, CasaXPS loads the default element library from within the same directory as the one in which the CasaXPS.exe executable file is located. The name of the default element

library file is CasaXPS.lib and is designed with the view that the element library can be constructed for specific applications. For example, in the case of quadrupole MS, a library consisting of elemental isotopes is appropriate to the resolution of quadrupole mass spectra, while for high resolution ToF MS a library consisting of entries for molecular fragments is required when assigning mass peaks.

Preparing an element library file for mass spectra may be performed using a spreadsheet program such as Excel or tools on the Exact Mass Calculator property page allowing correctly formatted library files to be constructed from lists of chemical formulae. Methods for displaying the significant peaks based on selections from an element library constructed from one or more library files are described below.

### The Element Library and Linking ToF Peaks for Display

High resolution ToF spectra typically consist of numerous peaks; however for some analyses only a small number of correlated peaks are significant for distinguishing between samples; a peak at one mass is only characteristic of a particular compound when also accompanied by other peaks in the spectrum. A strong link between the element library and displaying data for inspection is therefore introduced in CasaXPS 2.3.15. The objective is to use the element library to specify a set of mass peaks grouped with respect to correlated peaks which are used to makes selections of VAMAS blocks. These selections of VAMAS blocks containing narrow interval mass spectra combine with the display tools in CasaXPS to provide a perspective in which overall spectral distribution and localised peak structure can be assessed with relative ease.

A ToF data set presented as a set of unit mass VAMAS blocks can be viewed in the more traditional form of a single plot. The traditional perspective of a ToF spectrum is achieve by selecting all the VAMAS blocks in the right-hand pane, then pressing the overlay toolbar button. When viewed as a single continuous display, all the features for manipulating the display are still open for use.


The advantage of creating a set of mass calibrated VAMAS files is that the spectrum can be dissected and displayed with a variety of options: Display only those peaks more than 5% in intensity of the largest peak.



Display one VAMAS block per tile for those peaks greater than 5% of the maximum peak. All peaks scaled with respect to a specific peak; mass 23 in this case.



Scale the peaks on an individual basis.



Take a closer look at specific peaks.



Enhancements for manipulating the selection and display for ToF MS data are available on the Element Table property page of the Element Library dialog window.



The mechanisms offered on the Element Table property page are described in the following sections.

#### Linking Element Library Entries

A CasaXPS library file may be prepared with a set of entries corresponding to particular sample chemistry. Such a library file can be loaded or merged with the existing library file whenever appropriate. The essential feature of the entries in the given library file is that a set of mass formulae are all assigned the same unique string for the Transition column.



#### Using the Selection Mechanism

By way of example, a set of formulae only involving carbon and hydrogen are assigned the Transition string **CH**. On selecting one of the entries using the Name column of the table on the Element Table property page bearing the **CH** Transition string before pressing the **Display Linked VBs** button on the Element Table property page causes all those VAMAS blocks (in the experiment frame with focus) to be displayed in the left-hand pane, one VAMAS block per tile. Thus, a set of related mass peaks can be easily displayed for inspection.



A dialog window provides a means of only selecting those VAMAS blocks for which the peak intensity is greater than the specified percentage of the maximum peak in the data.

MS Peak Threshold		×
From Selected VAMAS	6 Blocks	OK
Threshold	5	

The key used to match the VAMAS blocks in the experiment frame is the string corresponding to the Species VAMAS field within each VAMAS block. The Species VAMAS field is used in the header string for each column of blocks in the right-hand pane of the experiment frame.

48 -	<u>n   48,   1</u>	<u>n 1</u>		2						
10	21	22	23	24	25	26	27	28	29	30
20	21	- 22	23	24	25	26	27	- 28 -	- 29	30

The ToF spectral files, when split into sets of VAMAS blocks, are created using the appropriate nominal masses to create these Species fields and the library entries with the common Transition library field are used to compute the corresponding nominal mass for each library entry, which when matched to the Species VAMAS fields causes the data to be displayed in the tile list.



🔲 Element Li	ibrar <b>y</b>			. 🗆 🗙
Element Table	Periodic Ta	ble   Input Fil	e Exact Mass	
Name	Mass	Element	Transition	_
CHICI	12	12	CH	
CH(C+H)	13.0078	13	CH	_
CH[C+H <sup>*</sup> 2]	14.0156	14	CH	
CHIC+H*31	15.0235	15	CH	
F[F]	18.9984	19	F 💻	
CH[C*2+H	26.0156	26	CH	
CH[C*2+H	27.0235	27	CH	
CH[C*2+H	28.0313	28	CH	
CO[C+H+0]	29.0027	29	CO	
CHIC*2+H	29.0391	29	CH	
CO[C+H*2	30.0105	30	C0	
	30.0469			
	30.9984	31		✓
C Zoom Wł	nen Line Seleo	cted	Find Pe	aks
🗌 🗌 Create W	hen Line Sele	cted		
🔲 Use Libra	ry FWHM		Create Re	gions
Clear A	Il Elements	E	dit Block Species/	Trans
		Ec	dit Source Analyse	r Angle
#T + #T ·	Overlag	y Linked VBs	Display Link	ed VBs

The element library file also includes Transition strings CO and F.

The different assignments for the Transition strings are simply a partition of the file between three possible sets of mass peaks; however a more realistic example might involve significant peaks from any combination of mass peaks, all of which would be collectively assigned a common Transition string. Should the same mass peak correspond to more than one compound, the element library file can include repeated entries differing only by the Transition string.

#### **Overlaying Related VAMAS Blocks**

The Element Table property page also includes a button for overlaying VAMAS blocks selected from the current file using the same mechanism as the **Display Linked VBs** button described above.



To overlay a set of VAMAS blocks corresponding to a predefined compound, one of the entries in the element-table list for the compound is selected before pressing the **Overlay Linked VBs** button. A dialog window appears offering a threshold value, which represents the percentage of the maximum height intensity of the peaks in the experiment frame. Only peaks of intensity greater than the percentage specified on the dialog window will be included in the set of VAMAS blocks overlaid in the active tile.

### Constructing an Element Library File

The element library file was constructed using the **Ex M T** button on the Exact Mass property page and three text files containing lists of chemical formulae. An example file containing formulae used to compute exact masses for library entries is as follows.



To create a corresponding library file, select the text file via the File Dialog invoked by the **Ex M T** button.

Element Library	
Create Mass Table from Formulae File	? 🛛
Look in: 🗀 Library Files	• 🗈 💣 📰 -
CasaXPS_mass.lib E F.txt CH.lib Formulae.txt CH.txt CO.lib Co.txt F.lib	
File <u>n</u> ame: F.txt	<u>O</u> pen
Files of type: All Files (*.*)	Cancel
Delete Entry Clear Markers Delete All Zoom Create	Find Peaks Load Regions Create Peaks

The base-name for the text file is used to assign a string to the Transition field in the resulting library file created when the Open button is pressed on the File Dialog window. The new library file appears in the directory where the original text file is located.

🔀 N	licrosoft	Excel - F.I	ib								
8	Eile Edit	<u>V</u> iew <u>I</u> n	sert F <u>o</u> rmat	<u>T</u> ools <u>D</u> a	ata <u>W</u> indov	v <u>H</u> elp A	cro <u>b</u> at	Type a	question for l	nelp 👻 -	.8×
	🛩 🔜 🛛	3 🔁 🧉	🗟 🖤 🖻	n • •	Σ - 2	100%	• 🕐	B %	;00 A -		» •
1	ta ta l	2 🔁 🖄	2 🖪 😥	Reply w	ith <u>C</u> hanges.	End Revie	n 🖕				
	7										
	A1	-	<i>f</i> ∗ 1								
	А	B	С	D	E	F	G	Н		J	-
1		1									
2	1	F	F[F]	1.90E+01	KE	1.90E+01	-1.00E+00	LA(5,4.8,0	1.00E+02	Ion Gun	
3	3	1 F	F[C+F]	3.10E+01	KE	3.10E+01	-1.00E+00	LA(5,4.8,0	1.00E+02	Ion Gun	
4	3	2 F	F[C+H+F]	3.20E+01	KE	3.20E+01	-1.00E+00	LA(5,4.8,0	1.00E+02	Ion Gun	
5	3	3 F	F[C+H*2+I	3.30E+01	KE	3.30E+01	-1.00E+00	LA(5,4.8,0	1.00E+02	Ion Gun	
6											_
7	• H\E						4				ЪĽ
Read	ly	/									

The intension is that a text file is prepared for those mass fragments characteristic of a particular compound, from which a library file is then created. When it is desired to visually inspect a ToF spectrum for evidence of the given compound, the library file for the compound is loaded into CasaXPS via the Input File property page.

Element Library		
Element Table   Periodic Table	Input File Exact Mass	1
Browse	Write Lib	
File Type		
CasaXPS lib	C Kratos lib	
C SSI Type 1	C SSI Type 2	
C KAL lib	C Simple Table	
C RBD Table	C VG Av. Scofield	
C VG Av. Wagner	C JEOL AES	
Load	Merge	

The library file displayed via the Element Table scrolled list

🔲 Element L	Element Library							
Element Table	Periodic Ta	ble   Inpu	t File Exac	t Mass				
Name	Mass	Time B	n Rel.At	ound. Line Sh				
CH[C]	12	-1	10	IO LA(5,4.8				
CH[C+H]	13.0078	-1	10	IO LA(5,4.8				
CH[C+H*2]	14.0156	-1	10	IO LA(5,4.8				
CH[C+H*3]	15.0235	-1	10	IO LA(5,4.8				
F[F]	18.9984	-1	10	10 LA(5,4.8				
CH[C*2+H	26.0156	-1	10	10 LA(5,4.8				
CH[C*2+H	27.0235	-1	10	i0 LA(5,4.8				
CH[C*2+H	28.0313	-1	10	10 LA(5,4.8				
CO[C+H+O]	29.0027	-1	10	IO LA(5,4.8				
CH[C*2+H	29.0391	-1	10	10 LA(5,4.8				
CO[C+H*2	30.0105	-1	10	10 LA(5,4.8				
CH[C*2+H	30.0469	-1	10	IO LA(5,4.8	×			
<				>				
🗖 Zoom Wł	nen Line Seleo	cted		Find Peaks				
📃 🖂 Create W	'hen Line Sele	cted			- L			
🔲 Use Libra	ry FWHM		_	Create Regions				
Clear A	Clear All Elements Edit Block Species/Trans							
1	124.212 : 0 Edit Source Analyser Angle							
#T + #T -	Overla	y Linked V	Bs Di	isplay Linked VB	s			

is a combination of loading three different library files using the Input File property sheet. The first file was selected using the **Browse** button, and then pressing the **Load** button caused the selected library file to replace the existing library entries. The two remaining files were merged with the first file by again using the **Browse** button to select the files followed by pressing the **Merge** button.

### Examining the Peak Structure using Zoom Actions

The standard method for defining a range of intensities in CasaXPS is to use the left-mouse button to drag a box over the peaks of interest before leftclicking inside the box on the display tile. The mechanism used in the definition of the zoom-box is enhanced when the Element Table property page is top-most on the Element Library dialog window. These enhancements are enabled by holding down the Control Key or the Control Key at the same time as the Shift Key on the key board. The result of combining the Control Key with the Element Table top-most on the Element Library dialog window is to create a narrow and tall zoom box at the location of the cursor whenever the left-mouse button is clicked.



The second modification to the zoom mechanism is designed to provide a means of creating a limited intensity applicable to the mass range currently in effect. Holding down the Control Key at the same time as the Shift Key alters the behaviour of the mouse drag action such that the zoom box always extends over the current mass range, but permits the height of the box to be determined from the cursor's final position.



To perform the zoom action, click inside the zoom box.

While zoom-actions permit a global perspective of a spectrum to be transformed into the display of a specific peak, there is always a cost associated with mouse actions required when transforming the display to see the peaks located at a nominal mass. The problem lies in the sparse nature of the mass peaks compared to the number of data bins comprising a spectrum. It is for this reason that the nominal masses can be broken down into individual VAMAS blocks using the **Display Linked VBs** button on the Element Table property page described above, thus offering a means of individually displaying a user defined set of VAMAS blocks. When these blocks are displayed, each spectrum appears such that the intensity scale is appropriate for each and every VAMAS block. However, while ensuring the peak structures are visible, the relative scale of these data, when viewed as individually scaled tiles, is lost. For this reason new SIMS toolbar buttons are introduced to permit the intensity scale for the entire set of data displayed in the left-hand pane of an experiment frame to be determined from the active tile. These toolbar buttons when coupled with the extension to the number of tiles per row, from four to ten, allows the peak structures within each VAMAS block to be visualized with a similar perspective of intensity as that seen in an overlaid plot of the data. The following display shows two rows of VAMAS blocks after scaling with respect to the tile with heading 43.



The Page Tile Format dialog window provides the means of adjusting the number of tiles per row and the Tile Display Parameter dialog window offers display settings for switching the tile display to those seen. The organization of the VAMAS blocks in the scrolled list means that paging down the scroll list effectively scrolls through the mass range in the spectrum being displayed.

The enhanced Page Tile Format window provides the means of changing the number of tiles per scroll position in the left-hand pane of the experiment frame.

Page Tile Format	
1 2 3 4 12 13 14	5         6         7         8         9         10         11           15         16         28         32         36         40
Tiles Arranged in	TilesperRow/Column C1 C2 C3 C4 C5 C6 C7 C8 C9 ⊙ 10
Number of Rows/Columns	C 1 C 2 C 3 C 4 C 5 C 6 C 7 C 8 C 9 C 10 C 1 C 2 C 3 C 4 C 5 C 6 C 7 C 8 C 9 C 10 C 1 C 2 C 3 C 4 C 5 C 6 C 7 C 8 C 9 C 10 C 1 C 2 C 3 C 4 C 5 C 6 C 7 C 8 C 9 C 10
J	OK Cancel Apply

To display the VAMAS blocks without an x-axis, the Tile Display Parameters dialog window is used.

Tile Display Parameters	
XAxis   YAxis   Geometry   Display   Colours   Global	
Independent Variable	
C Binding Energy Binding Energy (eV)	Font
Kinetic Energy     Mass (u)	
🔽 Display Axis Label	
Min 42.3637116101152 Max 43.6322895198752	
🔽 Display Minor Tick-Marks 🗌 Manual Axis Scale 🛛 3	
Display Axis Scale [0, 0] (0, 0)	
Set Scale (1,1)	
T Rescale Axis	
OK Cancel	Apply

# **Profiling Features for ToF data**



Figure 28 ToF Mass Spectrum displayed using Time Bins. Data provided by Prof. Winograd, Pennsylvania State University, USA.

ToF MS is often categorized according to the method for generating the ions from the sample. The data in Figure 28 is an example of Secondary Ion Mass Spectrometry SIMS, where the ToF technique is used to separate ions with different mass-to-charge ratio following exposing the sample to a focused beam of ions from an ion gun. Since the beam from the ion-gun can be scanned across the sample surface, ToF data may be collected over a set of points on the sample. Knowledge of where on the sample a time event was recorded allows the spectral data in Figure 28 to be assigned to pixels in mass resolved images as seen in Figure 29. These images in Figure 29 correspond to the peaks identified in Figure 28, that is, each image is obtained by only counting time-events contributing to the peaks labelled on the spectrum.



Figure 29: Mass resolved images extracted from the ToF SIMS data file corresponding to the histogram Figure 28.

Similarly, identifying pixels in an image and only counting time-events corresponding to the selected pixels permits multiple spectra to be extracted from a single ToF data file. Given the complex nature of ToF spectra, the ability to retrospectively examine the data from an experiment is a powerful tool in understanding the information in the spectra.

ToF MS is used to obtain spectra through ionization mechanisms other than SIMS. Proton Transfer Reactor (PTR) ToF MS (Figure 30) provides a soft ionization mechanism of an analyte by the transfer of a proton from  $H_3O^+$  to the analyte. While spatial information is not appropriate for PTR ToF MS, the technique provides temporally separation of spectra, where variation of mass-peaks with time provides a profile (Figure 31) of changes in a sample.



Figure 30: Schematic of a PTR ToF MS (Kore Technology Limited, UK)

The tools for the purpose of visualizing the data from a ToF MS experiment are described in following sections.

## **ToF Data File Options**



The options on the SIMS toolbar for manipulating ToF MS data fall into two categories: those for which a new VAMAS file is created without reference to other data and those for which an existing spectrum or image is used to create spectra or images representing a subset of the data within a file.



Figure 31: A profile of PTR ToF MS peaks.

Currently, two types of file formats may be processed using these options: Kore Technology Limited list files and Prof Winograd's (Pennsylvania State University) Bio ToF XYT files. Both types of files contain time information as well as associating the time information with image pixels.

The first step to viewing a data file is to create a spectrum from the entire file of time values regardless of whether the file is a set of images or a profile of some description. From the total spectrum, peaks are identified from which images or profiles are created. In turn, the images or profiles can be used to define the pixels or layers of interest, which once specified are used to extra pixel or layer filtered spectra from the original data file.

### Create a Total Ion Spectrum 🖄

A total ion spectrum is created from a data file specified using the resulting File Dialog window shown in Figure 32.

Convert to V	AMAS file				? 🗙
Look in: 🔀	TestProfile	•	] 🕁 [	* 🖻	<b></b>
031406 ps 031406 ps 031406 ps 031406 ps 031406 ps 031406 ps 031406 ps	u dp run 104'.xyt u dp run 1001.xyt u dp run 1002.xyt u dp run 1003.xyt u dp run 1004.xyt u dp run 1005.xyt	1031406 psu dp ru 1031406 psu dp ru 1031406 psu dp ru	ın 1006.: ın 1007.: ın 1008.:	xyt xyt xyt	
File <u>n</u> ame:	031406 psu dp ru	n 1001 xyt			<u>O</u> pen
Files of type:	PSU Files (* xyt)		•	]	Cancel

Figure 32: Convert to VAMAS File Dialog window used to specify the ToF MS files.

The file types supported are:

1) Files with the extension "Ist" created using by the Kore Technology Ltd ToF MS instruments. The Ist files contain a list of binary data in which each analysis ToF cycle appears as a sequence of start events followed by a list of stop events representing ions arriving at the detector. While these analysis cycles may be associated with a pixel in an image or a layer of a profile, the spectrum created from the Ist file ignores these distinctions and generates a single time histogram from the timing information. Images or profiles are subsequently generating from the list file using the total spectrum as a reference.

2) Files with the extension "xyt" created from the Penn State University Bio ToF instrument. The xyt files are binary files containing a two dimensional array of lists, where each pixel in an image is associated with a list of stop events specifying the arrival times of ions at the detector. The total ion spectrum is created by ignoring the spatial information and generating a histogram from the entire set of time lists.

3) Files with the extension "spc" generated from the Kore Technology Ltd instruments. These spc files are already in the form of a time binned

histogram. No image or profile information is present in these files. Sets of spc files within a directory can be profiles using the options below.

4) Files with the extension "dat" generated from the Penn State University Bio ToF instrument. The dat files are already in the format of a time binned histogram. No image or profile information is present in these files. Sets of dat files within a directory can be profiles using the options below.

Creating a time spectrum from a raw data file  $\checkmark$  involves selecting the file with the appropriate file extension using the File Dialog window shown in Figure 32. Once a file is converted and displayed in an experiment frame, the data can be selectively processed using information defined on the total ion spectrum.



Figure 33: Total Ion Spectrum from an Image File.

The spectrum in Figure 33 is a total ion histogram which is mass calibrated and prepared with quantification regions in anticipation of processing a set of images from the raw list file. The quantification regions define the time intervals over which ions are allocated to pixels in images as the list file is processed a second time. Figure 34 represents the outcome to the second pass through the list file; the images are obtained from the second pass by only collecting and allocating counts to images in accordance with the quantification regions define on the spectrum in Figure 33.



Figure 34: Images processed from the list file corresponding to Figure 33.

The steps taken to create these images will now be described.

# Create Images from Spectra using Quantification Regions

Once a total ion spectrum is available, the data can be mass calibrated using one of two procedures: 1) define a set of calibration points in the form of (time, mass) pairs via the Exact Mass Calculator on the Element Library dialog window or 2) define a set of calibration regions using the Quantification Parameters dialog window and calibrate the spectrum using a button from the SIMS toolbar. While it is not necessary to calibrate the time bin spectrum before generating images, given a time-to-mass calibration the automatic region creation option on the Element Library dialog window will assign the nominal mass to the region names and therefore aids the interpretation of the data.

#### Defining Quantification Regions using the Find Peak buttons

Regions defined on the total ion spectrum provide the time intervals over which counts are accumulated into images. The Quantification parameters dialog window permits regions to be created one at a time, however ToF MS is typically blessed with numerous peaks and creating a region for each of these peaks manually would be too time-consuming. As a result, the Element Table and Periodic Table property pages offer Find Peak buttons, which for ToF data will create a region for each peak subject to a threshold criterion.

While the regions are created by simply pressing the Find Peaks button on the Element Table property page, it is worth reviewing the limits of the regions using the Reset  $\rightarrow \leftarrow$  and Zoom Out  $\leftarrow$  toolbar buttons. When the Reset button is pressed, any regions created on a spectrum are loaded onto the zoom-list. Thus pressing Reset followed by repeatedly pressing the Zoom Out button will step through the regions created by the Find Peaks button. The limits for the regions can be adjusted under mouse control provided the Region property page is visible on the Quantification Parameters dialog window.

🔲 Quantifica	🗖 Quantification Parameters 🛛 🔲 🔀						
Regions Components Data Editor Benort Spec BPT Benort							
	periorite   p			[	1		
Wide			[	Calc Max			
· · · · · · · · · · · · · · · · · · ·							
Regions	A	В	C	D 🔨			
Name	27	29	39	41			
R.S.F.	1	1	1	1			
Start	95790	99190	114002	11673			
End	96187	99523	114306	11705			
BG Type	Zero	Zero	Zero	Zero			
Av. Width	0	0	0	0			
St. Offset	0	0	0	0			
End Offset	0	0	0	0			
Cross Se	299,54	299,54	299,54	299,5			
Tag	NoTag	NoTag	NoTag	NoTa			
Area	174266	51982.2	32581.7	60076			
Std Dev	0	0	0	0			
fwhm	396.36	332.256	303.536	325.28			
Position	96047	99404	114159	11685			
% Conce	54.48	1.63	1.02	1.88			
Max Height	5237.0	212.0	148.0	238.0			
Min Height	2556.0	97.0	71.0	109.0 💌			
<u>&lt;</u>				>			
Create	Cal	culate Error B	ars [	Delete			
Create From Labels Save Regions Copy and Paste							
Intensity Calibration Copy Names							
Automatic 0 Update stol por port							
	1		STO	RCL RST			

#### Creating the Images

The total ion spectrum retains a record on the file from which it originated, therefore pressing the toolbar button with toolbar hint *List File to Images* will cause the original list-file to be scanned a further time. During the second scan of the list file, counts are accumulated into images defined by the current set of regions on the spectrum displayed in the active tile. Note, regions created automatically may be numerous and therefore the resulting image data file is potentially large. The operation is similarly potentially time consuming and may take several tens of seconds, depending on: the number

of regions as well as the processor power, memory and disk speed of the PC performing the operation.

The spectrum in Figure 33 was used to create the images displayed in Figure 34 via the stoolbar button.

# Spectra Generated from Image Zones

Given an image of the sample, a false colour scale defined over intensity ranges offer a means of specifying which pixels from the image should be included in the procedure for creating time-bin histograms from the list file. As a result, one or more spectra can be extracted from the list file which will be referred to as LUT spectra (Look-Up Table); the colour used to display a pixel in a false colour image is defined using a "look-up table" of colour values.

The image in Figure 35 is an example of a mass resolved image displayed using a false-colour-scale consisting of four colours. The intensity scale is partitioned into the false colours defined using intensity ranges characteristic of the implanted gallium lettering PSU and the complementary pixels to the gallium lettering. Four spectra are generated from the list file based on the four false colours defined on the image by only collecting time events corresponding to the pixels displayed using the false colours. A comparison of these LUT spectra for the gallium mass range is made in Figure 36.





The procedure for generating LUT spectra is as follows:

- 1. Select an image generated from the original total ion spectrum for a list file.
- 2. On the Image Processing dialog window, available from the Options menu, select the Colour Scales property page.





3. Select the False radio button from the Scale Type list and press the Apply button.

Image Processing				
Image Processing Colour Scales Image Quantification	VAMAS Info			
Autoscale Limits      Below Threshold = Blue     Refresh     Scale Type     Grey      Thermal      Coloured      Bi-colour      False     Colog				
Limits May Min	Apply			
Scale: 2.12592515034516 2.8630131	3576304e-006			
Red: 100 0				
Green: 100 0				
Blue: 100				
Define False Colour Zone Order False Colours Spectrum Index (vb30,194) Intensity = 0.0214641	Add False Colour			

- 4. Mark a range on the image colour scale displayed next to the image in the left-hand-side of the experiment frame using the cursor whilst holding down the left-mouse-button.
- 5. Press the button labelled **Add False Colour**. The colours, as specified by the dialog window which appears when the button is pressed, are displayed in the colour scale in the active tile and the image itself is updated using the newly define false colour.

The default false colours are ordered to agree with the colours used to display spectra when overlaid in a tile.

6. Once the desired zones of pixels are assigned false colours, the image can be made the current template using the **Define Image** on the Image Processing property page.



7. To generate the LUT spectra press the toolbar button. The list file corresponding to the image is scanned and, for each false colour in the image defined by the previous step, a spectrum is added to a new experiment frame.

# Creating a Profile from a Total Ion Spectrum

The concept of a ToF list-file is applicable to time dependent measurements where spectra evolve during the course of an experiment. The data from such an experiment can be treated as a total ion spectrum. Just as the data from an image can be interpreted as a large area analysis to produce a single spectrum from all the data, so too can all the ToF timing information be interpreted as a single spectrum; the difference being that, in creating the total ion spectrum the for a profile, all the changes over time are ignored.



Figure 37: PTR ToF MS total ion data showing quantification regions prepared for the purpose of creating time-dependent intensity profiles.

The total ion spectrum in Figure37 provides a coarse description of the experiment, from which the time dependent information can be extracted. The procedure used to plot the variation of the spectra with time is similar to that of extracting images from an image list file, that is, quantification regions are assigned to the mass-peaks on the total ion spectrum followed by pressing the toolbar button. The total ion spectrum maintains a reference to the original list-file, therefore on pressing the toolbar button, the list-file is scanned a second time producing a trace for each quantification region defined on the total ion spectrum.



Figure 38: A plot of three traces from the regions defined on the total ion spectrum in Figure 37.

The data in Figure 38 represents three quantification regions from the regions defined on the total ion spectrum in Figure 37. The oscillations in the profiles are due to changes in the air sampled from a subject whilst the mastication of food is performed.



Figure 39: Spectra generated from the regions defined on the profile in Figure 38.

Given a profile such as the one on Figure 38, spectra corresponding to a range of times or cycles can be generated as illustrated in Figure 39. For each quantification region defined on a profile, (Figure 38 includes two such regions) a spectrum is obtained by summing only those times falling into the ranges specified by the regions.

Quantification regions are added to a profile using the Quantification Parameter dialog window. Given the two regions in Figure 38, pressing the

toolbar button causes the list-file to be read a further time accumulating the spectra from the timing data. The spectra in Figure 39 are examples of data collected from layers within a profile experiment.

### Create a Profile from a Directory of Files

So far, ToF list files have been considered as the data structure managing images of spectra or profiles of spectra. The extension to the concept of a list

file is a directory of list files, where each list file represents a change in terms of the experiment performed. For example a depth profile of image list files offers the possibility of measuring an image of spectra for each layer within a sputter depth profile. The experimental conditions evolving during the course of the experiment are the depth beneath the surface at which an image of spectra is acquired. Such experiments are by nature time consuming and large in data size.

Creating a profile from a directory of list files involves selecting a representative spectrum from the directory of list files suitable for specifying the mass calibration and also the set of peaks to be profiled throughout the directory of files.

The active tile must display a spectrum for which regions are defined suitable for mass calibration. Once the spectrum is prepared the process is initiated via the 2toolbar button. A File Dialog window allows the specification of a data directory containing the files for which the list files are processed as follows:

- 1. Converted to spectrum VAMAS files.
- 2. Each spectrum is mass calibrated using the regions defined on the spectrum in the active tile.
- 3. Peaks identified using an automatic threshold search and regions created for each of these peaks identified.
- 4. The region intensities are collected into profile traces for each region created in the peak identification step.
- 5. A new experiment frame created using the name specified on the File dialog window.

Initially the directory of list files appears as follows.

Convert to V.	AMAS file		? 🔀
Look in: 🗀	Raw Data for XY	T Depth Profile 🔄 🗲 🔁	💣 🎟 •
031406 psu 031406 psu 031406 psu 031406 psu 031406 psu 031406 psu 031406 psu	dp run0104.xyt dp run1001.xyt dp run1002.xyt dp run1003.xyt dp run1004.xyt dp run1005.xyt	031406 psu dp run1006.xyt         031406 psu dp run1007.xyt         031406 psu dp run1008.xyt         031406 psu dp run1008.xyt         031406 psu dp run1009.xyt         031406 psu dp run1009.xyt         031406 psu dp run1010.xyt         031406 psu dp run1011.xyt	031406 psu c     031406 psu c
<			>
File <u>n</u> ame:	depth_profile.xyt		<u>O</u> pen
Files of <u>type</u> :	All Files (*.*)	•	Cancel

Each file with the directory is processed during the course of the profile procedure. On completion, the same directory appears with a VAMAS file corresponding to each original list file plus one further VAMAS file containing the profile traces for each peak identified as significant. After processing the directory appears as follows.

Convert to V	AMAS file		? 🔀
Look in: 🔎	XYT Depth Profile	1	r 🗄
031406 psi 031406 psi 031406 psi 031406 psi 031406 psi 031406 psi 031406 psi	u dp run1032.xyt u dp run1032.xyt.vms u dp run1033.xyt u dp run1033.xyt.vms u dp run1034.xyt u dp run1034.xyt.vms	I depth_profile.xyt.vms	
<			
File <u>n</u> ame:	depth_profile.xyt		<u>O</u> pen
Files of type:	All Files (*.*)	•	Cancel

Before pressing the Profile from Files itoolbar button, a spectrum must be displayed in the active tile prepared with regions sufficient to provide an adequate mass calibration.



The file name for the profile with the appropriate list-file extension, entered in the Filename text-field on the File dialog window, specifies the type of list files in the current directory and on pressing the Open button, the profiling operation is initiated. These files tend to be large; therefore the time taken to complete the profiling task may be large too.

When the profile is complete, a new experiment frame opens in CasaXPS and the profile traces are displayed. A typical profile file will contain numerous profile traces.



## Convert and Merge a Directory of XYT File

An alternative to automatic profiling a directory of list files is to analyses the depth profile using the set of total-ion spectra converted from each XYT file in a directory.



A profile experiment, in which a sequence of images is acquired into separate XYT files, can be investigated in terms of the total ion spectra using the investigated in terms of the total ion spectra using the images button. A File Dialog window is used to specify both the directory containing the XYT files and the name of the file created by scanning the directory for XYT files; the XYT files are individually converting into VAMAS files containing the total ion spectra. After each XYT file in the directory is converted, the set of VAMAS files are merged into a new experiment frame.



Figure 40: Merged XYT files

To load a directory of XYT files into a new experiment frame, select the toolbar button to invoke a File Dialog window; move to the directory containing the XYT files then enter a name into the file name text-field with the file extension ".xyt". ToF spectra tend to require large quantities of memory, therefore take care not to attempt to merge an excessive number of file as the operation may take considerable time to complete.

Once a set of spectra are loaded into an experiment frame, trends within the data can be assessed using the Custom Report mechanism on the Report Spec property page of the Quantification Parameters dialog window shown in Figure 40. A set of profiles determined from the data in Figure 40 are displayed in Figure 41. These profiles are obtained by defining a set of quantification regions using the Regions property page, generating an Area Report using the Custom Report on the Report Spec property page then creating a new VAMAS file from the tabulated report via the **Create Profile** menu option on the File menu.



Figure 41: Profiles generated from the merged spectra shown in Figure 40.

## Image Depth Profile Data Analysis

Given a directory of xyt files:

Create an experiment frame containing a profile set of images corresponding to the set of regions defined on a spectrum in the active tile.



Figure 42: Set of images created by accumulating counts into pixels based on regions defined on a spectrum.



Figure 43: Spectrum used to create images in Figure 42.

The images displayed in Figure 42 were generated from a directory of XYT files, where data from the XYT files are processed only for those counts falling within the time windows specified by regions defined on the associated spectrum in Figure 43.

Three regions were defined using a total ion spectrum. The spectrum must be displayed in the active tile before pressing the  $\textcircled$  toolbar button. The operation involves reading the entire set of XYT files in the directory specified via the File Dialog window. The process is potentially time consuming. To process a directory of XYT files, a file name must be specified in the File name text-field on the File Dialog with extension .xyt. On completion, a new VAMAS file is created with the name specified concatenated with the .vms file extension.



Figure 44: False colour image used to generate profiles in Figure 45.

The Image Processing dialog window on the Options menu offers tools for processing these sets of images. For example, the false colour image scale defined on the image displayed in Figure 44 may be used to generate depth profiles for the sum of pixel based on coloured zones.



Figure 45: Profiles constructed from a directory of XYT files using the false colour image in Figrue 44.

Creating the profiles in Figure 45 requires the generation of LUT spectra from the directory of XYT files. Regions defined on the LUT spectra coupled with the Custom Report on the Report Spec property page of the Quantification Parameters dialog window provide to tools to create the profiles based on false colours.



Figure 46: Spectra collected using the false colour image in Figure 44.

#### Generating LUT Spectra from a Directory of List Files

### 🛎 Spectra from False Colour Zones

Given a directory of XYT files and a false colour image, the **b** toolbar button creates a new experiment frame containing a set of spectra from each XYT file, where the spectra are accumulated from the time information from only those pixels identified by the false colours in the image. For example, the false colour image in Figure 44 is the sum of all the gallium 69 isotope images and therefore the colour zones are determined by the gallium distributed throughout the volume sampled by the depth profile. Spectra from these four colour zones are collected into the new experiment frame shown in Figure 46, thus the depth profile can be examined from the perspective of gallium using these spectra.

# **Quantification Reports and ToF Data**

The intensity associated with a ToF mass spectrum represent ions counted at a detector. The time element of the measurement is less important than is the case for other techniques where a specific data channel is monitored for a specified time; data under these measurement conditions are typically quantified in terms of counts per second (CPS). For ToF Data, the pulsed extraction of ions and the delay required to allow ions to traverse the flight tube result in a departure from the need to consider counts per second, but rather to focus on the number of ions detected. CasaXPS generally assumes data are quantified in terms of CPS and peak areas are integrated with respect to the independent variable. Since the default quantification regime in CasaXPS is not appropriate for ToF data, there are ToF motivated configuration options to permit quantification of ToF intensities in terms of a summation of counts over time or mass bins.

# Quantification via the Report Spec Property Page

The Report Spec property page of the Quantification Parameters dialog window offers two methods for generating quantification reports. The Standard Report is predominantly aimed at tabulating results on a spectrumby-spectrum basis; while the Custom Report is designed to support the profiling of data acquired sequentially, for example a depth profile.

Quantification Parameters
Regions Components Data Editor Report Spec. RPT Report
Standard Reports     Image: Comps     Use Config File       Regions     Comps     Use Profile Format       Regions and Comps     Combined With Tags
Custom Report Quantification Item Names C24H'3 GA Sa
Regions         Comps         All         Clear           Ratio Region         Ratio Comp         Ratio All         Clear
Names     Formula       C°24H°3     C°44H°3       C4H°3     C4H°3       Ga     Ga       Na     Na
Area Report Height Report Tag Defined Report

#### **Standard Report**

The Standard Report permits quantification in terms of quantification regions and/or synthetic components. For ToF data, quantification based on number of ions requires the specification of appropriate configuration files. These configuration files are located in the directory called CasaXPS.DEF.



Standard Reports		🔽 Use Config File
Regions	Comps	Use Profile Format
Regions and Com	ps	Combined With Tags

Generating a quantification report for ToF data requires the use of ASCII configuration files named:

Report Button Pressed	Configuration File Name
Quantification Regions	RegionQuantTable.txt
Synthetic Line shapes	ComponentQuantTable.txt
Regions and Comps	RegionComponentQuantTable.txt

The configuration files can be edited using Notepad or any other text based editor.

×

The format for the files is a list of keywords entered one per line, where each keyword specifies the type of information appearing in each column of the text quantification report generated when the corresponding button on the Standard Report is pressed.

CasaXPS Licensed to:A1 CASA - [CasaXP5]		
📴 Elle View Window Options Select Help		_ & ×
		8
	💉 🎼 💱 🗣 🖾 🗖 🖾 🖼 BG 🛼 🚛 🛗 🗱 🐼 💯 🛼 🍕	by 🚄 Root
	( v v	2 <b>2 2</b>
	Justification Parameters     Image: Sec. RPT Report       Standard Reports     Image: Sec. RPT Report       Standard Reports     Image: Sec. RPT Report       Regions     Comps       Regions and Comps     Combined Web Tags       Custom Report     Image: Sec. RPT Report       Image: Sec. RPT Report     Image: Sec.	Image         Image <th< th=""></th<>
	Regions         Comps         All         Clear         23           Ratio Region         Ratio Comp         Ratio All         24         25	LUTO LUTI LUT2 LUT3 LUTO LUTI LUT2 LUT3 LUTO LUTI LUT2 LUT3 LUTO LUTI LUT2 LUT3
10 <sup>1</sup> 0	Name         Formals         27           C72+H'3         C2+H'3         28           C+H'3         C+H'3         29           Ga         Ga         30           Na         Na         31           34         34         34	UT0         UT1         UT2         UT3
10 20 30 40 50 60 80 Mass (amu) [time plot]	Area Report Height Report Tag Defined Report	

A quantification report is created for those VAMAS blocks selected on the right-hand pane of the experiment frame with focus.

LUT O	LUT 1	LUT 2	LUT 3
LUT 0	LUT 1	LUT 2	LUT 3
LUT 0	LUT 1	LUT 2	LUT 3
LUT 0	LUT 1	LUT 2	LUT 3
LUT 0	LUT 1	LUT 2	LUT 3
	LUT 0 LUT 0 LUT 0 LUT 0 LUT 0	LUT 0 LUT 1 LUT 0 LUT 1 LUT 0 LUT 1 LUT 0 LUT 1 LUT 0 LUT 1	LUT 0         LUT 1         LUT 2           LUT 0         LUT 1         LUT 2

On pressing the Regions button from the Standard Report section with the Use Config File tick-box tricked, the following report is produced:

🙆 CasaXPS Licensed to:A1 CASA	- [CasaXP5:2]				
File Window Fonts Help					_ & ×
					2
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Sample Id	Block Id	Name	Position	Total Charge	
031406 psu dp run1004_lutspectra.vms	LUT O	C+H*3	15.0295	10576	
031406 psu dp run1004_lutspectra.vms	LUT 0	Na	22.9925	47876	
031406 psu dp run1004_lutspectra.vms	LUT 0	Ga	68.9462	2804	
031406 psu dp run1004_lutspectra.vms	LUT O	C*2+H*3	27.0263	27933	
031406 psu dp run1004_lutspectra.vms	LUT 1	C+H*3	15.0278	1302	
031406 psu dp run1004_lutspectra.vms	LUT 1	Na	22.9927	19512	
031406 psu dp run1004_lutspectra.vms	LUT 1	Ga	68.9382	8328	
031406 psu dp run1004_lutspectra.vms	LUT 1	C*2+H*3	27.0264	6205	
031406 psu dp run1004_lutspectra.vms	LUT 2	C+H*3	15.0298	180	
031406 psu dp run1004_lutspectra.vms	LUT 2	Na	22.9928	3189	
031406 psu dp run1004_lutspectra.vms	LUT 2	Ga	68.9424	2720	
031406 psu dp run1004_lutspectra.vms	LUT 2	C*2+H*3	27.0241	938	
031406 psu dp run1004_lutspectra.vms	LUT 3	C+H*3	15.0283	73	
031406 psu dp run1004_lutspectra.vms	LUT 3	Na	22,9904	1539	
031406 psu dp run1004_lutspectra.vms	LUT 3	Ga	68.9430	6730	
031406 psu dp run1004_lutspectra.vms	LUT 3	C*2+H*3	27.0237	437	
		RegionQuantTable.txt - I	Notepad 📃 🗖 🔀		
	File	Edit Format View Help			
	VAI VAI NAI PO: SII	MAS_BLOCK_SAMPLE_ID MAS_BLOCK_NAME ME SITION MS_PEAK_AREA			
	<		► .::		

For ToF data, the important column is the one specified using the keyword **SIMS\_PEAK\_AREA** in the RegionQuantTable.txt configuration file. The columns in the quantification report have a one-to-one correspondence with the keywords entered in order one-per-line within the RegionQuantTable.txt file.

The quantification report is exported as a tab spaced ASCII data set through the clipboard. To move the quantification report to a spreadsheet, for example, press the Copy button on the top toolbar. A clipboard dialog window offers the option to save the data to file or copy the data onto the clipboard.

A		
CasaXPS Licensed to:A1 C/	,ASA - [CasaXP5:2]	
File Window Fonts Help		
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Sample Id	Block Id Name Position Total Charge	
031406 psu dp run1004_lutspectra		
031406 psu dp run1004_lutspectra.	Clipboard Selection	
031465 psu dn run (09-) Litspetra 031465 psu dn run (09-) Litspetra	Sample IdBlock Id Name         Position         Total Drage           03146 pru do na1004, Litzpecta vm: LUT 0         C-H13         15.0256         10576           03146 pru do na1004, Litzpecta vm: LUT 0         Na         22.932         17976           03146 pru do na1004, Litzpecta vm: LUT 0         Na         22.932         17976           03146 pru do na1004, Litzpecta vm: LUT 0         Na         22.932         17976           03146 pru do na1004, Litzpecta vm: LUT 0         C-4472         20.631         2333           03146 pru do na1004, Litzpecta vm: LUT 0         C-4472         150.276         1302           03146 pru do na1004, Litzpecta vm: LUT 1         Ca         68.9382         6236           03146 pru do na1004, Litzpecta vm: LUT 1         Ca         27.0034         6206           03146 pru do na1004, Litzpecta vm: LUT 1         Ca         82.932         1616           03146 pru do na1004, Litzpecta vm: LUT 2         Na         22.9323         1616           03146 pru do na1004, Litzpecta vm: LUT 2         Na         22.9324         163           03146 pru do na1004, Litzpecta vm: LUT 2         Na         22.930         163           03146 pru do na1004, Litzpecta vm: LUT 2         Na         22.931         150.23           03146 pru do nan0004, Litzpec	
		<u>a</u>
	DK Save Copy Selection to Clipboard Copy All to Clipboard	

69

The data on the clipboard can be pasted into another program such as Excel.

Henre     Interf     Page layout     Formulation     Data     Reverse     View     Image layout     Image layou
Image: Second
Clipboard G Fant G Aligoment G Number G Styles Cells Editing
3 Sample Id Block Id Name Position Total Charge
4 031406 psu dp run1004_lutspectra.vms LUT 0 C+H*3 15.0295 10576
5 031406 psu dp run1004_lutspectra.vms LUT 0 Na 22.9925 47876
6 031406 psu dp run1004_lutspectra.vms LUT 0 Ga 68.9462 2804
7 031406 psu dp run1004_lutspectra.vms LUT 0 C*2+H*3 27.0263 27933
8 031406 psu dp run1004_lutspectra.vms LUT 1 C+H*3 15.0278 1302
9 031406 psu dp run1004_lutspectra.vms LUT 1 Na 22.9927 19512
10 031406 psu dp run1004_lutspectra.vms LUT 1 Ga 68.9382 8328
11 031406 psu dp run1004_lutspectra.vms LUT 1 C*2+H*3 27.0264 6205
12 031406 psu dp run1004_lutspectra.vms LUT 2 C+H*3 15.0298 180
13 031406 psu dp run1004_lutspectra.vms LUT 2 Na 22.9928 3189
14 031406 psu dp run1004_lutspectra.vms LUT 2 Ga 68.9424 2720
15 031406 psu dp run1004_lutspectra.vms LUT 2 C*2+H*3 27.0241 938
16 031406 psu dp run1004_lutspectra.vms LUT 3 C+H*3 15.0283 73
17 031406 psu dp run1004_lutspectra.vms LUT 3 Na 22.9904 1539
18 031406 psu dp run1004 lutspectra.vms LUT 3 Ga 68.943 6730
H + + H Sheet1 / Sheet2 / Sheet3 / 1

#### **Custom Report**

The profiles in Figure 45 were created using quantification regions and the Custom Report section on the Report Spec property page.

🗖 Quantification Parameters
Regions       Components       Data Editor       Report Spec.       RPT Report         Standard Reports       Image: Comps       Image: Comps       Image: Comps       Image: Comps         Regions       Comps       Image: Comps       Image: Comps       Image: Comps       Image: Comps         Regions       and Comps       Combined With Tags       Image: Combined With Tags       Image: Combined With Tags
Custom Report Quantification Item Names C*2+H*3 C+H*3 Ga Na
Regions     Comps     All       Ratio Region     Ratio Comp     Ratio All
Names         Formula           C*2+H*3         C*2+H*3           C+H*3         C+H*3           Ga         Ga           Na         Na
Area Report Height Report Tag Defined Report

Since ToF intensities are determined from the number of ions within a peak and not the peak area, quantification items defined on the spectra, either regions or components, must include a keyword in the Tag field and the report must be generated using the Tag Defined Report button. To indicate that a region or component derives from ToFSIMS data, the keyword **tofsims** must be entered in the Tag field for the quantification item.

Quantifica	tion Para	meters		
Regions Con	nponents D	ata Editor   F	Report Spec.	RPT Report
			r	Calc Max
Regions	A	В	C	~
Name	C+H*3	Na	Ga	C*2
R.S.F.	1	1	1	
Start	20368.7	24084	38715.2	257
End	20576.6	24367.2	38746	26(
BG Type	Zero	Zero	Zero	Z
Av. Width	1	1	1	
St. Offset	0	0	0	
End Offset	0	0	0	=
Cross Se	299,54	299,54	299,54	299,5
Tag	tofsims	tofsims	tofsims	tof
Area	1301.9	19511.1	8283.7	62
Std Dev	U	U	U	
twhm	6.93922	5.66173	8.40337	5.4
Position	20423	24221	38726	25
% Conce	3.69	55.27	23.47	
Max Height	142.0	2/15.0	832.0	8,
Min Height	0.0	0.0	2.0	
				>
Create	Cal	culate Error B	ars	Delete
Create Fro	m Labels	Save Region	ns Copy	and Paste
Intensity Ca	alibration			nou Names
- Automa	tic 0			Apprivanios
Adding		Upda	STO	BCL BST

The Tag Defined Report button uses the keyword in the Tag field to determine the type of data to retrieve from the quantification item. The keyword **tofsims** causes the summation of the counts within the region or under the components on a bin-by-bin basis. Other keywords include **height**, which returns the maximum peak height as the measure for intensity. Note: for both keywords **tofsims** and **height**, the intensities are divided by the value entered in the RSF field; therefore the number of ions recorded for a given peak is only obtained for an RSF of unity.

A further word of warning: the Custom Report is defined in terms of a list of names and formulae. The formulae are constructed from the name fields used to specify the quantification items. There is no difference between how regions and components are treated within these formulae, both are considered to be quantification items and intensities from regions and/or components can be combined to create a quantification report. A key property of the Custom Report is that, intensities from either regions or components or both with the same name field are automatically summed together. To be sure that the profile is from exactly the intended items, *always use different names for items included in the profile*.

# An Overview of Working with ToF Data in CasaXPS

The SIMS toolbar is displayed via the View menu on CasaXPS.



The SIMS toolbar offers a range of options for displaying and manipulating ToF MS data.

**Display Options:** 

|--|

ToF Time to Mass Calibration Options:

Tof Taf 💁

Organization of Data:

Data Conversion Options:

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# SIMS Toolbar Buttons: Display Options

The toolbar button switches the display setting between forcing data to be displayed with a lower intensity of zero and allowing a selectable lower limit. The default state for the display of ToF MS spectra is to force a lower limit of zero. A line is drawn at the bottom of the tile to indicate when the display is forced to plot intensities above zero intensity. When the line appears at the bottom of the tile displaying the ToF spectrum, a zoom box drawn over the display will only indicate the upper limit for the purposes of expanding the display.


On left-clicking inside the zoom box with the zero base line active the display becomes:



Toggles the display between log and linear display modes:



## Cverlay selected VAMAS blocks by column:



Given a selection of VAMAS blocks in the right-hand pane, display each column of VAMAS blocks in separate tiles in the left-hand pane. Each tile is scaled with respect to the spectra displayed within the tile.

Adjust the scale for the tiles displayed in the left-hand pane with respect to the intensity range determined from the active tile.



Adjust the scale for the tiles displayed in the left-hand pane with respect to the intensity range currently used in the active tile and toggle the mode for the y-axis display.









A spectrum displayed in the active tile changes the mass range used to view the data each time the H toolbar button is pressed. The mass range is always anchored by the smaller mass limit and with each press of the button the size of the display range cycles between 5 amu, 10 amu, 25 amu, 50 amu and 100 amu.

Step the mass range towards higher mass values or towards lower mass values. The current mass range determines the size of the step. On

pressing either toolbar button, the mass range is stepped by half the interval currently being displayed.



Expand the display range about the central mass defined for the active tile. The SIMS toolbar button increases the mass range about the central mass for each press of the button without rescaling the intensity range. The equivalent button on the second toolbar performs the same operation as the SIMS toolbar button with the exception that the button on the second toolbar also rescales the intensity range.



HE Step the current mass range by one amu. The intensity scale is unaltered by pressing either of these buttons.



Given a spectrum displayed in the active tile, the toolbar button adds a set of tiles to the scrolled list of tiles in the left-hand pane, where the display range in the active tile is split into sub-ranges, the number of which is define on the dialog window invoked by the toolbar button. The display before pressing the toolbar button:

CasaXPS   icensed to:A1 CASA - [1.ion_regions]	
File View Window Options Select Help	
The main hand the state water to the second se	
50 100 150 200 250 300 350 400 450	<del></del>
C. IN THE	
Spiit The	
ОК	
Cancel	
Number of your New Te	

Result of splitting the full spectrum into eight sub-ranges, one per tile is shown below:



Each sub-range is rescaled within the display tile. Note that if the number of tiles exceeds the number of tiles-per-page in the left-hand pane, the additional tiles cause the scroll-list to expand indicating the existence of further pages of display tiles.



# SNMS in CasaXPS

## An Overview

Sputtered Neutrals Mass Spectrometry (SNMS), as a technique related to SIMS, is supported on the Dynamic SIMS dialog window of CasaXPS.

The Dynamic SIMS property page is available from the SIMS toolbar The SIMS toolbar is displayed using the View menu on the CasaXPS Main Window menu bar.



Quantification of SNMS profiles requires the calculation of sensitivity factors. These SFs are calculated using options on the SNMS RSF Calculator property page.

Dynamic	SIMS				
Calibration	NMS RSF Calc	ulator Prep.	are Profiles		
SNMS	RSF Calculator				
Cu					
- Stand	ard &Weight O	% Atomic	% 0.2		_
Mass	per Mole (g)	3.549		Update V	alues
Signal	sotopic Mass 6	2.9296	Intensity	(CPS) 294.	999
Name	l % Wt	% Atomic	Mass p	SF	Isotope 🔨
Cu	0.2		63.549	0.263396	62.929
NI	51.5		58.7018 51.9957	1.7050 0.445540	57.335
V	0.22		50.9415	0.327895	50.944
<					>
Add	fissing Element	Ca	alculate SFs	Calcul	late RSFs
SNMS	Quantification — e Nano metres	1	Сор	y RSF to Sel	lected VBs
Ator	MC &M	922 %			

Relative SFs are SFs normalised with respect to a given isotope. Both SFs and RSFs are determined based on measurements from standard materials. Once established for a set of isotopes, data measured under identical conditions can be quantified in terms of either Atomic concentration or Mass concentration using options on the SNMS RSF Calculator property page. Further tools for transferring RSFs to other measurements are available on the Prepare Profile property page.

alibration   SNMS RSF Cal	Iculator Prepare Profiles
Select Matching Block	Select and Display Matching Blocks           Overlaid in the Active Tile
Block Id Cu Ni Cr V Mo Co Co V Fe	Match String Mass 63 Mass 58 Mass 52 Mass 51 Mass 98 Mass 59 Mass 184 Mass 56
SNMS Quantification I Use Nanometres Atomic % by File	Copy RSFs to Matching Selected VBs Copy Sputter Rates to All Selected VBs Mass % by File

The function of the Prepare Profile property page is to copy RSF and sputterrates to multiple data files with the view to generating quantified profiles from the raw SNMS data. The buttons on the Prepare Profile property page are designed to work based on selections made within the set of opened files. To this end, other buttons on the Prepare Profile property page provide a means to make selections appropriate for the action buttons.

SNMS and Dynamic SIMS are specified in CasaXPS using an identical framework. The RSF and sputter-rates are assigned on a measurement-cycle by measurement-cycle basis. In both SNMS and Dynamic SIMS, a profile fully prepared for quantification must have each cycle populated with RSF and sputter-rates as viewed via the Calibration property page of the Dynamic SIMS dialog window.

The sputter-rate for a given profile is calculated using the Calibration property page and, using the same mechanisms as for Dynamic SIMS, the

sputter-rate and appropriate RSF entries are updated. The table on the Calibration property page displays the parameters used during quantification.

Dynamic SIMS					
Calibration SNMS RSF	Calculator   I	Prepare Profile	es		
Define Interface D	efine Matrix	Ref. Signa	I Ni (1		
Define Suff/BG	Matrix In	Interface	RSF	Sputter	
Dose (atoms/cm2):	Cu [0] Cu [0] Cu [0]	Cu (0) Cu (0) Cu (0)	1.7565 1.7565 1.7565	5.2233e 5.2233e 5.2233e	5
Depth (nm):	Cu (0) Cu (0) Cu (0)	Cu (0) Cu (0) Cu (0)	1.7565 1.7565 1.7565	5.2233e 5.2233e 5.2233e	5 5 5
Subtract BG	Cu [0] Cu [0] Cu [0]	Cu (0) Cu (0) Cu (0)	1.7565 1.7565 1.7565	5.2233e 5.2233e 5.2233e	5 5 <b>⊻</b>
Elemental RSF					
🔲 Use Ref. Signal	Bulk Doped	d (atoms/cm3)	1.0000e	+000	_
Compute RSF	🔲 Use Bu	ulk Doped	Compute S	putter Rate	
RSF: 1.7565e+0	00	Sputter Rat	e (cm/s):	5.2233e-005	
Apply RSF/SR to Mat	rix Apply	RSF/SR to I	nterface	Restore RSF/	SR
Depth Profile Calibration	n				
Calibrate Depth F	Profile	🔽 Normalise	to Matrix	nterface Statis	tics
Calibrate All Pro	files	🔽 Use Nand	o metres	Profile Statistic	25

## **Basics of CasaXPS**

#### **Converting Data**

CasaXPS native file format is ISO 14976 VAMAS file. CasaXPS contains many conversion filters available from the Convert menu option on the File menu or via the top toolbar.

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0 🖻	<b>1</b>	

Converting data involves selecting the data file with the appropriate file extension via the Convert to VAMAS file dialog window.

Convert to V	AMAS file		? 🔀
Look jn: 🔎	Raw Data	▼ ← €	- 📸 🎟 -
Hastelloy s	et 1 with Co.csv teel set 1 with Co.csv		
File <u>n</u> ame:	Hastelloy set 1 with Co.csv		<u>O</u> pen
Files of <u>type</u> :	All Files (*.*)	•	Cancel

For example, Hiden data is saved in comma separated format with file extension csv. On selecting a file containing Hiden data format with the extension csv, CasaXPS will convert the data to VAMAS format and write a new file into the same directory as the original csv file.

Convert to V	VAMAS file	? 🛛
Look in: 🔎	) Raw Data 🔍 🗲 🖪	È 💣 🎟 -
Hastelloy s Phastelloy s Stainless S	set 1 with Co.csv set 1 with co.csv.vms Steel set 1 with Co.csv	
File <u>n</u> ame:		<u>O</u> pen
Files of <u>type</u> :	All Files (*.*)	Cancel

The VAMAS file will then open as an Experiment Frame in CasaXPS.



#### **Data Viewed Via an Experiment Frame**

A profile experiment contains one or more traces measured and recorded for each isotope monitored. The Experiment Frame in CasaXPS displays the data using two panes with an adjustable central divider. The left-hand-pane displays the data in graphical form.



The right-hand pane offers the data blocks within the VAMAS file.



The right-hand pane is used to make selections from the set of VAMAS blocks held within the VAMAS file. These selections are used to display subsets of data within the file and direct processing operations to specific data blocks.

### **Displaying Data**

Individual VAMAS blocks appearing in the right-hand pane are displayed by double-clicking the left-hand-mouse button with the cursor over the data block.



Selecting more than one VAMAS block in the right-hand pane and using the Overlay toolbar button causes the selected VAMAS blocks to be displayed in the active display tile.



## **Selecting VAMAS Blocks**

Selections are made using the right-hand pane:

- 1. Single click the left mouse button over the right-hand pane to select a single block of data.
- 2. Hold the Shift-Key down and single click the left mouse button over a different block in the right-hand pane to make a range selection.



- 3. To add to or remove from the current set of selected VAMAS blocks, hold the Control-Key down before left clicking the mouse with the cursor over a VAMAS block in the right-hand pane.
- 4. Use the Select menu to extend a selection to other VAMAS blocks of similar identity in other files.

1	Select	Help	
ì	Mov	e Left	
-	Mov	e Right	
1	Mov	eup	
	Mov	e Down	
2	Step	Slice Up	Ctrl+Page Up
l	Step	Slice Down	Ctrl+Page Dn
1	Rese	et Slice Index	Ctrl+Home
-	Step	Ordinate Up	Shft+Page Up
	Step	) Ordinate Down	Shft+Page Dn
	Rese	et Ordinate Index	Shft+Home
1	Last	Ordinate Index	Shft+End
	Nex	t Exp Var	Ctrl+F1
	Prev	rious Exp Var	
	Sele	ct All Blocks	Ctrl+F3
	Sele	ct All Matching Blocks	Ctrl+F4
1	Sele	ct and Display Matching Blocks	Ctrl+F5
	Sele	ct All Matching Block Ids	Ctrl+F6
	Sele	ct and Display Matching Block Ids	Ctrl+F7
	Sele	ct Blocks with Components	Ctrl+F9
	Cycl	e VAMAS File Index	Ctrl+F8

#### **Tile Display Options**

The left-hand pane of an Experiment Frame displays the data in the form of profiles, spectra or images. Options affecting the display are managed using the Tile Display Parameters dialog window. The Tile Display Parameters dialog window is invoked via the top toolbar



When plotting a profile involving multiple traces, a common requirement is to place a Legend or Key within the tile in which the data are plotted. The Display property page on the Tile Parameter dialog window provides control over placing a Key on either the right-hand side of the graph area or alternatively the left side via the **Draw Key** and **Key on Left** tick-boxes.

Tile Display Parameters
X Axis   Y Axis   Geometry   Display   Colours   Global   Display Items
Title Use Id Title   Vamas Block Comment Synthetic Components   Acquisition Parameters Residual   Annotation Spectrum Background   Exclude Annot. Tables Normalise Residual   Quant. Region Labels Draw Box on Header   Component Labels Axes Major Lines   Vert. Quant. Region Labels Draw Graph Box   Half Tile Display Draw Points   Draw Key Key on Left   Display Comps from First Spectrum Dashed Comps   Display Spectrum Index Dashed Lines   VB Comment First Tile Only
Ni Font
OK Cancel Apply



The Display property page also allows the profiles to be plotted using lines, points or both lines and points.

#### **Display Colours**

The colours used to plot the profiles are specifies using the Colours property page on the Tile Display Parameters dialog window.

Tile Display Parameters	
XAxis YAxis Geometry Display Colours Global	
Tile Background       Residual Trace         3D Background       Spectra         Region Background       Spectra Background         3D Fill       Synthetic Components         Colour Components using Comp Index       Combine Comp Index         Fill Combined Components       Fill Combined Spectra         Components Displayed as Background       Spectra	
OK Ca	ncel <u>Apply</u>

To modify the colours used to display the profiles, press the button on the Colours property page on the Tile Display Parameters dialog window labelled Spectra. Use the Colour dialog window to adjust the Custom Colours palette before pressing the OK button on the Colour dialog window followed by Apply or OK on the Tile Display Parameters dialog.

Color	? 🛛
Basic colors:	
	1
	Hu <u>e</u> : 0 <u>R</u> ed: 213
	Sat: 240 Green: 0
Define Custom Colors >>	ColorISolid Lum: 100 Blue: 0
OK Cancel	Add to Custom Colors

The order for the colours used to display the profiles is determined by the Custom Colours moving left to right then top to bottom as view on the Colours dialog window. Further, the order of the VAMAS blocks displayed in the Active Tile is determined by the order in which the data blocks are selected in the right-hand pane.



Holding the Control Key down allows the order of the data blocks to change and therefore the colours change accordingly.



## Calculating SNMS Sensitivity Factors

The task of calculating a set of sensitivity factors for SNMS requires a standard sample of known composition and a measurement from the standard sample, where a specific set of isotopes for which sensitivity factors are to be determined is used to monitor the sample-composition in terms of counts per second. The SNMS RSF Calculator determines a set of factors relating the amount of substance to the signal measured. Thus these sensitivity factors provide the scaling factors to convert measured signal to amount of substance for profiles measured from samples of unknown material composition. The calculation of SNMS sensitivity factors is performed using the SNMS RSF Calculator property page on the Dynamic SIMS dialog window.



An example of a standard sample is a Hastelloy material for which the composition is known to be:

Element	t % Composition by	
	Weight	
Cu	0.2	
Ni	51.5	
Cr	16.15	
V	0.22	
Мо	17.1	
Со	1.5	
W	4.29	
Fe	7.3	

When measured using a quadrupole mass spectrometer, the recorded signal from the Hastelloy sample defines the instrumental response for the given sample composition.



Armed with the experimental data measured from the standard and the table of material compositions, the sensitivity factors for the isotopes used in the experiment are calculated by populating the table on the SNMS RSF Calculator property page and defining a quantification region for each VAMAS block. The quantification region provides a means of estimating representative signal intensity for each profile.

🗖 D	ynamic SI/	٨S				🛛			
Cali	bration SNI	4S RSF Cale	ulator Prep	are Profiles					
			1 .						
	SNMS RSF Calculator								
	Cr								
	Standard			a. 🗖					
	• %	Weight 🔘	% Atomic	~ 0					
	Mass pe	r Mole (g)	0		Update Va	lues			
		,							
	Signal Iso	opic Mass 🛛	)	Intensity	(CPS) 0				
		,			,				
	Name	_ % Wt	% Atomic	Mass p	SF 1	Isotope ^			
	Ni	ŏ	0	0	1	õ 🔳			
	Mo	0	0	0	1	0 💌			
	<					>			
	Add Miss	ina Element	c	alculate SFs	Calcula	te RSFs			
		-							
	SNMS Quantification								
	User	ano metres		Co	py RSF to Sele	cted VBs			
	Atomic		flass %						

The information used to calculate the sensitivity factors is recorded in the VAMAS blocks for each of the profiles. It is therefore necessary to update the appropriate information for each of the VAMAS blocks representing the data measured from the standard sample.

None	Ма							
1	Cu	Ni	Cr	V	Mo	Co	W	Fe

To update the information needed to compute the sensitivity factors, repeat the following steps for each isotope in the SNMS profile measured from the standard sample.

1. Double-click a VAMAS block in the right-hand pane.

None		Ma	Ma	Ma	Ma	Ma	Ma	Ma	Ma	
1		Cu	Ni	Cr	٧	Mo	Co	W	Fe	
D	ynamic	SIMS								×
Cal	ibration	SNMS RSF	Calcula	tor Pre	pare Prol	iiles				
	SNMS	RSF Calcul	ator							
	Cu									
	Stand	lard								
	۰	% Weight	0%	Atomic	%	0				
	Mass	per Mole (g	a) (				Update 1	Values		
	Signal	Isotopic Ma	0 226		Inte	ensity (CF	PS) 0			
	Name Cu	0 % WI	: ;	& Atomic	Mass 0	p S	F	lsotop 0	e	
	<								>	
	Add	dissing Eler	nent	(	Calculate	SFs	Calc	ulate RS	Fs	
	SNMS	Quantificati se Nano me	on stres			Copy F	SF to S	elected \	/Bs	
	Ator	mic %	Mas	\$%						

2. Select the type of percentage known about the composition of the sample and enter the value for the percentage in the text-field.

🗖 Dynamic SIMS
Calibration SNMS RSF Calculator Prepare Profiles
SNMS RSF Calculator
- Chundred
% Weight C % Atomic % 0.2
Mass per Mole (g) Update Values
Signal Isotopic Mass 0 Intensity (CPS) 0
Name         % Wt         % Atomic         Mass p         SF         Isotope           Cu         0         0         0         1         0
Add Missing Element Calculate SFs Calculate RSFs
SNMS Quantification           FV         Use Nano metres         Copy RSF to Selected VBs           Atomic %         Mass %

The Update Value button becomes active as soon as a value is entered for the percentage composition.

3. Check that the correct mass per mole and isotopic mass are displayed and press the Update Value button.

The table on the property page displays the values currently available for profiles displayed in the active tile.

🗖 Dynamic SIMS 📃 🗖 📘									
Calibration SNMS RSF Calculator Prepare Profiles									
SNMS RSF Calculator									
Image: State									
Signal Isotopic Mass 62.9296 Intensity (CPS)									
Name % Wt % Atomic Mass p SF Isotope									
Add Missing Element Calculate SFs Calculate RSFs									
SNMS Quantification           Iso Nano metres         Copy RSF to Selected VBs           Atomic %         Mass %									

The mass per mole is determined from the average mass for a given element, while the isotopic mass represents the mass of the peak used to measure the profile signal.

The table is only updated when the Update Values button is pressed.

Each VAMAS block holding the data from a profile must be updated with the composition information. Overlaying the VAMAS blocks for the full profile in the active tile causes the table on the SNMS RSF Calculator to display the full list of quantification information.



The table reflects the percentage composition for the standard sample. To relate these percentage compositions to the signal intensities for the set of profiles, it is necessary to specify a representative intensity for each isotope. The representative intensity is determined as the average over a set of acquisition cycles as specified via a quantification region. Specifically, the signal intensity is the average intensity over the set of data cycles defined by the first quantification region for each VAMAS block in the experiment.

4. Create a quantification region for each VAMAS block, where the limits to the region define a set of data channels over which the intensity can be averaged and assumed to be representative of the signal measured for the isotope being profiled.

The quickest means of creating quantification regions on SNMS/SIMS data is to use the Calibration property page on the Dynamic SIMS dialog window.

Dynamic SIMS							
Calibration SNMS R	6F Calculator   Prepare Profiles						
Define Interface	Define Matrix Ref. Signal	Cu (0)					
Define Surf/BG	Matrix In Interface RS	F Sputter C 🔨					
Dose (atoms/cm2):	Cu[0] Cu[0] 1 Cu[0] Cu[0] 1	5.2233e 1 5.2233e 1					
1.0000e+000	Cu[0] Cu[0] 1	5.2233e 1					
Depth (nm):	Cu[0] Cu[0] 1 Cu[0] Cu[0] 1	5.2233e 1 5.2233e 1 5.2232- 1					
4.0000e+002	Cu[0] Cu[0] 1	5.2233e 1					
Subtract BG	Cu (0) Cu (0) 1 Cu (0) Cu (0) 1	5.2233e 1					
🔲 Elemental RSF	<						
🔲 Use Ref. Signal	Bulk Doped (atoms/cm3): 1	0000e+000					
Compute RSF	Use Bulk Doped Cor	npute Sputter Rate					
RSF: 1.0000e	+000 Sputter Rate (cm	/s): 5.2233e-005					
Apply RSF/SR to	Apply RSF/SR to Interfa	ice Restore RSF/SR					
Depth Profile Calib	ation						
Calibrate Depth Profile Vormalise to Matrix Interface Statistics							
Calibrate All	Profiles 🔽 Use Nano met	res Profile Statistics					

Overlay all the VAMAS blocks in the active tile before pressing the Define Surf/BG button on the Calibration property page.



The Define Surf/BG button creates two quantification regions per VAMAS block overlaid in the active tile. Only the first region, assigned the name Peak, is used to determine the signal intensity for the SNMS data. The reason two regions are created is to allow dynamic SIMS experiments to define a surface zone and a zone representative of the background signal to a SIMS profile.

The quantification regions are so named because of their use in XPS data analysis. For the purposes of SIMS and SNMS, the regions only define intervals. Should these intervals need changing from the default values obtained by pressing the Define Surf/BG button, the Regions property page on the Quantification Parameters dialog window provides a means of making changes to these interval limits.



Each VAMAS block must be updated with any changes to the region limits. Quantification regions are propagated from one VAMAS block to others by selecting the range of VAMAS blocks in the right-hand pane of the experiment frame and right-clicking the mouse over the left-hand pane displaying the data with the modified regions. A dialog window appears offering the ability to propagate the regions to other VAMAS blocks listed on the dialog.

Browser Operations		X
Propagate Propagate Propagate Propagate Propagate Propagate Propagate Propagate	Processing     Annotation     Error Bars	OK Cancel
Match Species/Trar	isition	
Quantification		
• None C F	Regions 🔿 Comps 🔿 Combined	
Source: Cu		
Selected Block Id.	File Name	
Cu	hastelloy set 1 with co.csv.vms : c:\documents and	settings\neal\my
Cr	hastellov set 1 with co.csv.vms : c:\documents and	settings\neal\my
V	hastelloy set 1 with co.csv.vms : c:\documents and	settings\neal\my
Mo	hastelloy set 1 with co.csv.vms : c:\documents and	settings\neal\my
	hastelloy set 1 with colcsy.vms : c:\documents and hastelloy set 1 with colcsy.vms : c:\documents and	settings\neal\my
Fe	hastelloy set 1 with co.csv.vms : c:\documents and	settings\neal\my
<		>

Tick the tick-box in the propagate section and press the OK button. A further dialog window appears requesting confirmation, which should be accepted by pressing the Yes button.

CasaXPS	
⚠	You are about to propagate regions/components to spectra of different Element/Transition.
	Continue?
	<u>Y</u> es <u>N</u> o

Assuming that the background region is deleted and the Peak region adjusted to provide a representative average signal from each profile, the appearance of the set of profiles changes as follows.



Following the creation of an appropriate quantification region, the SNMS RSF Calculator property page will show the average value determined from the region for the first VAMAS block displayed in the active tile.



The VAMAS file for the standard sample is now ready to calculate the sensitivity factors for the measured isotopes.

VAMAS blocks used in the calculation of the sensitivity factors must be:

- 1. All overlaid in the active tile
- 2. The table on the SNMS RSF Calculator property page displays the correct percentage compositions , Mass per Mole and signal isotopic mass
- 3. A region is defined on each VAMAS block.

Once the data are prepared appropriately, pressing the Calculate SF button calculates and adds sensitivity factors to the table on the property page.

		Calcu	late S	Fs				
ynamic SIM	s							
ibration SNM	IS RSF Ca	lculator Pre	pare Profiles	1				
SNMS RSF	Calculator							
Cu								
Standard								
€ %\	Veight C	X Atomic	× 0.2	2				
Manager	Mala (a)	0.0 17 1.0						
mass per	Mass per Mole (g) 63.549 Update Values							
Signal Isote	opic Mass	62.9296	Intensi	ty (CPS) 29	8.117			
Signal Isoto	opic Mass	62.9296 & Atomic	Intensil	by (CPS) 29	8.117			
Signal Isoto Name Cu Ni	opic Mass 8 Wt 0.2 51.5	62.9296 & Atomic	Intensil Mass p 63.549 58.7018	y (CPS) 29 SF 0.259682 1.76426	8.117 Isotope ^ 62.9296 57.9353			
Signal Isotr Name Cu Ni Cr	opic Mass 2 Wt 0.2 51.5 16.15	62.9296	Mass p 63.549 58.7018 51.9957	y (CPS) 29 SF 0.259682 1.76426 0.445009	8.117 62.9296 57.9353 51.9405			
Signal Isoto Name Cu Ni Cr V	0pic Mass 0.2 51.5 16.15 0.22	62.9296	Intensil Mass p 63.549 58.7018 51.9957 50.9415	y (CPS) 29 SF 0.259682 1.76426 0.445009 0.328954	8.117 1sotope ^ 62.9296 = 57.9353 51.9405 50.944			
Signal Isoto Name Cu Ni Cr V V	opic Mass 0.2 51.5 16.15 0.22	62.9296	Intensi Mass p 63,549 58,7018 51,9957 50,9415	y (CPS) 29 SF 0.259682 1.76426 0.445009 0.328954	8.117 62.9296 57.9353 51.9405 50.944			
Signal Isoto Name Cu Ni Cr V Add Missi	opic Mass 0.2 51.5 16.15 0.22 ng Elemen	62.9296	Intensil Mass p 63,549 58,7018 51,9957 50,9415 Calculate SF	y (CPS) 29 SF 0.259682 1.76426 0.445009 0.328954 sCalc	8.117 62.9296 57.9353 51.9405 50.944 > ulate RSFs			
Signal Isote Cu Ni Cr V K Add Missi	opic Mass 2 Wt 0.2 51.5 16.15 0.22 ng Elemeni ntification	62.9296	Intensil 63.549 58.7018 51.9957 50.9415 Calculate SF	y (CPS) 29 SF 0.259692 1.76426 0.445009 0.328954 sCalc	8.117 62.9296 57.9353 51.9405 50.944			
Signal Isoto Cu Ni Cr V Add Missi SNMS Qua	opic Mass 2 Wt 0.2 51.5 16.15 0.22 ng Elemeni ntification ano metres	62.9296	Intensit 63,549 58,7018 51,9957 50,9415 Calculate SF	y (CPS) 29 SF 0.259682 1.76426 0.445009 0.328954 s Calc	8.117 62.9296 57.9353 51.9405 50.944			
Signal Isote Name Cu Ni Cr V V Add Missi SNMS Qua V Use N Atomic S	opic Mass 0.2 51.5 16.15 0.22 ng Elemeni ntification ano metres	62.9296	Intensi Mass p 63.549 58.7018 51.9957 50.9415 Calculate SF	y (CPS) 23 SF 0.259682 1.76426 0.44500 0.328954 Calc calc	8.117 62.9296 57.9353 51.9405 50.944 Julate RSFs elected VBs			

Alternatively, relative sensitivity factors are calculated by first selecting an entry in the Name column of the table before pressing the Calculate RSFs

🛛 Dynami	c SIMS					
Calibration	SNMS RSF Calo	culator Pre	oare Profiles			
SNM:	3 RSF Calculator					]
Star	ndard ∙ %Weight C	% Atomic	% 0.2			
Ma	ss per Mole (g)	63.549		Update	Values	
Sign	al Isotopic Mass 🛛	62.9296	Intensity	(CPS) 29	8.117	
Nam	ne %Wt	% Atomic	Mass p	SF	Isotope	
Mo	17.1		95.9219	2.64223	97.9054	
Co	1.5		58.9332	0.668902	58.9332 📩	
W	4.29		183.847	3.34633	183.951 📃	
Fe	7.3		55.8458	0.593691	55.9349 💌	
<					>	
,						
Add	I Missing Element		Calculate SFs	Calc	ulate RSFs	
SNM	S Quantification -					1
•	Use Nano metres		Co	py RSF to S	elected VBs	
A	omic %	Mass %				

A dialog window report the reference isotope by name and on pressing OK, the table is populated with RSF with respect to the indicated VAMAS block.



In both cases, the RSF or SF values are also entered into the VAMAS blocks on a cycle-by-cycle basis, which can be verified via the Calibration property page of the Dynamic SIMS dialog window.

Dynamic SIMS						K			
Calibration SNMS RSF	Calibration SNMS RSF Calculator Prepare Profiles								
Define Interface	efine Matrix	Ref. Signa	al   Ni [1]						
Define Surf/BG	Matrix In	Interface	BSE	Sputter					
Dose (atoms/cm2):	Cu [0]	Cu [0]	2.97168	1	5				
1.0000e+000	Cu [0]	Cu [0]	2.97168	i	5				
Depth (nm):	Cu [0]	Cu (0) Cu (0)	2.97168	1	5				
4.0000e+002	Cu (0) Cu (0)	Cu (0) Cu (0)	2.97168 2.97168	1 1	5				
Subtract BG	Cu (0) Cu (0)	Cu (0) Cu (0)	2.97168 2.97168	1 1	5 5 🛩				
🔲 Elemental RSF	<				>				
🔲 Use Ref. Signal	Bulk Doped	(atoms/cm3)	): 1.0000e	+000					
Compute RSF	🗐 Use Bu	lk Doped	Compute 9	putter Rate					
RSF: 4.3740e-00	01	Sputter Ra	te (cm/s):	1.0000e+00	0				
Apply RSF/SR to Ma	trix Apply	RSF/SR to I	nterface	Restore R	SF/SR				
Depth Profile Calibrati	on								
Calibrate Depth	Profile	Vormalise	e to Matrix	Interface St	atistics				
Calibrate All Pro	ofiles	🔽 Use Nan	o metres	Profile Stat	tistics				
L									

## **Quantification of SNMS Profiles**

Isotopic profiles are quantified by applying the sensitivity factors to the intensities measured from the sample. These sensitivity factors are maintained within profiles measured from standard materials of known composition. The quantification of a profile is therefore achieved by transferring the appropriate sensitivity factors from these standard materials to the unknown material, establishing the sputter-rate for the material under analysis, followed by calculation of the percentage atomic or mass concentrations. The result is a new experiment frame containing the quantified profile. The process will be illustrated by quantifying a stainless steel sample using sensitivity factors determined from a Hastelloy material of known composition.

#### **Quantification of Stainless Steel using SNMS: an Example**



On conversion, the data from a stainless steel sample appears in CasaXPS, viewed via the Calibration property page of the Dynamic SIMS dialog window, as a set of VAMAS blocks in the right-hand pane of an experiment frame.

None	Ма	Ма	Ма	Ма	Ма	Ма	Ма	Ма	
0	Cu	Ni	Cr	- V -	Mo	Co	W	Fe	Γ

The Calibration property page shows that initially the profiles are all assigned an RSF of unity and a unit sputter-rate.

Dynamic SIMS					
Calibration SNMS RSF	Calculator   F	Prepare Profi	les		,
Define Interface	efine Matrix	Ref. Sign	al Ni	[1]	
Define Surf/BG	Matrix In	Interface	RSF	Sputter	C 🔨
1.0000e+000	Cu [0] Cu [0] Cu [0]	Cu [0] Cu [0] Cu [0]	1	1	4
Depth (nm):	Cu [0] Cu [0] Cu [0]	Cu (0) Cu (0) Cu (0) Cu (0)	1	1	4
Subtract BG	Cu [0] Cu [0] Cu [0]	Cu (0) Cu (0) Cu (0)	1	1	4 4 4 🛩
Elemental RSF	Bulk Doped	l (atoms/cm3	3): 1.00	D0e+000	
Compute RSF	🔲 Use Bu	lk Doped	Compu	te Sputter Rat	e
RSF: 1.0000e+0	00	Sputter Ra	ate (cm/s)	1.0000e+0	100
Apply RSF/SR to Ma	trix Apply	RSF/SR to	Interface	Restore F	RSF/SR
Depth Profile Calibrati Calibrate Depth I	on Profile	🔽 Normalis	e to Matri	x Interface 9	itatistics
Calibrate All Pro	files	🔽 Use Nar	io metres	Profile St	atistics

RSFs and sputter-rates are defined on a cycle-by-cycle basis. This allows values to be adjusted depending on the point in a profile at which the intensities are measured. In multilayer materials permitting differing RSFs and sputter-rates may be important; however for a uniform stainless steel sample all cycles will be assigned the same RSFs and sputter-rates independent of depth.

The Prepare Profile property page on the Dynamic SIMS dialog window provides the tools for transferring RSFs and sputter-rates between profiles.

Dynamic SIMS		
Calibration SNMS RSF Cal	culator Prepare Profiles	
Select Matching Block	s Select and Display Matching Blocks	
Source ) (AMAS Ploaks C	luarlaid in the Active Tile	
Source VAMAS Blocks C		
Block Id Ni	Match String Mass 58	
Cr	Mass 52	
Cu	Mass 55 Mass 63	
V	Mass 51 Mass 99	
Co	Mass 50 Mass 59	
JW	Mass 184	
	Copy RSFs to Matching Selected VBs	
	Copy Sputter Rates to All Selected VBs	
SNMS Quantification-		
🔽 Use Nanometres		
Atomic % by File	Mass % by File	

To transfer the RSFs from the Hastelloy standard to calibrate a stainless steel sample:

1. Load both the Hastelloy profile (previously processed to include the sensitivity factors) and the stainless steel profile.

Data converted from Hiden files include VAMAS fields defining the element and species for the VAMAS blocks. While these strings are only important in as much as profiles from the same isotopic peaks must be assigned identical strings, the actual strings are at the users discretion. The Hiden data labels the mass peaks with the nominal mass such as "Mass 58". These element and transition strings are used to make global selections within the set of open VAMAS files; also the transfer of RSF and sputter-rate values is achieved via the Prepare Profile property page based on these strings. Therefore, a consistent assignment for these fields significantly aids the speed of data preparation leading to quantified profiles.

2. Tile the experiment frames within CasaXPS so that the right-hand panes can easily be seen



In this example only two files are in use so tiling the opened files using the Window menu is relatively easy. When more files are involved, a cascade of experiment frames can be more useful a means of monitoring the selections within the file set.

CasaXPS Licensed to:A1 CASA											
File View Window Options Select Help	_										
New Window     Cascade		- -	• / b	# <b>#</b>	8	1	5 B. 1	?			
Tile Arrange Icons	<u> </u>			G 558 <u>4</u> 里	Block Cont Info		<u>₽</u> ¶ <sub>R</sub> \\	을 <sup>ENT</sup>			
1 partial_calib_hastelloy set 1 with co.csv.vms     2 stainless steel set 1 with co.csv.vms				M 🐨 🛃							
Cu			None M	la Ma	Ma I	Иа Ма	a Ma	Ma I	Ma		
Dynamic SIMS					ur j	V P	10 0	W	re		
Calibration SNMS RSF Calculator Prepare Profiles	1										
Select Matching Blocks Select and Display Matching	Blocks								_		
			None 0	Ma Ma Cu Ni	Ma Cr	Ma I	Ma Ma. Mo Ci	Ma	Fe Fe		
Source VAMAS Blocks Overlaid in the Active Tile											
Block Id Match String Cu Mass 63	_										
Cr Mass 52 V Mass 51											
Mo Mass 98 Co Mass 59											
W Mass 184 Fe Mass 56											
Copy RSFs to Matching Selected	VBs										
Copy Sputter Rates to All Selecter	d VBs										
SNMS Quantification											
Atomic % bu File Mass % bu File											
						_					
		ngs\Nea	I(My Docu	ments\Workin	igDir\Hiden	\Hiden\Hid	len\SNMS\D	lata for Mar	ual\Raw D	ata\partial_ca	alib <u>.</u> //

- 3. Select the VAMAS blocks within the Hastelloy standard previously prepared with appropriate sensitivity factors.
- 4. Press the Select Matching Blocks button to match the selection from the Hastelloy experiment frame throughout the opened VAMAS files.



5. Ensure that the source experiment frame is the experiment frame with focus.



6. Press the Copy RSFs to Matching Selected VBs

button.

A dialog appears listing the set of VAMAS blocks together with the file names from which the VAMAS blocks belong.

Copy when Matched S	IMS/SNMS RSFs to Listed Blocks	×
partial_calib_hastelloy set	Cancel 1 with co.csv.vms : C:\Documents and Settings\Neal\My Documents\Wor	rkin
Selected Block Id.	File Name	~
Cu	partial calib hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Ni	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Cr	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
V	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Mo	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Co	- partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
W	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Fe	partial_calib_hastelloy set 1 with co.csv.vms : C:\Documents and Settings	
Cu	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	
Ni	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	
Cr	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	
V	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	-
Mo	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	
Co	stainless steel set 1 with co.csv.vms : c:\documents and settings\neal\my	~
<		

7. To transfer the RSF from the source file to the destination VAMAS blocks, press the OK button on the dialog.

The key point to note is that the RSFs are copied only to those VAMAS blocks for which the source VAMAS block element/species strings match the target element/species strings. To force the transfer of RSF values to other VAMAS blocks regardless of such constraints, use the button on the SNMS RSF Calculator property page.

ynamic s	IMS				
ibration S	NMS RSF Cal	culator Prep	are Profiles		
SNMS R	SF Calculator				
Cu					
- Standa	rd				
۲	% Weight 🔿	% Atomic	% 0.2		_
Mass	per Mole (g)	63.549		Update V	alues
Signal Is	otopic Mass	52.9296	Intensity	(CPS) 298	.117
Signal Is	otopic Mass	52.9296	Intensity	(CPS) 298	.117
Signal Is	otopic Mass	52.9296	Intensity Mass p	(CPS) 298	.117
Signal Is Name Cu Ni	otopic Mass	52.9296 & Atomic	Intensity Mass p 63.549 58.7018	(CPS) 298 SF 0.437401 2.97168	117 1sotope 62.929 57.935
Signal Is Name Cu Ni Cr	otopic Mass	52.9296 X Atomic  	Intensity Mass p 63.549 58.7018 51.9957	(CPS) 298 SF 0.437401 2.97168 0.749563	117 62.929 57.935 51.940!
Signal I: Name Cu Ni Cr V	**************************************	52.9296 % Atomic   	Mass p 63.549 58.7018 51.9957 50.9415	(CPS) 298 SF 0.437401 2.97168 0.749563 0.554082	117 62.929 57.935 51.940! 50.944 ❤
Signal Is Name Cu Ni Cr V	totopic Mass 2 Wt 0.2 51.5 16.15 0.22	52.9296	Intensity 63.549 58.7018 51.9957 50.9415	(CPS) 298 SF 0.437401 2.97168 0.749563 0.554082	117 62.929 57.935 51.940 50.944 ❤
Signal Is Name Cu Ni Cr V V	otopic Mass % Wt 0.2 51.5 16.15 0.22 ssing Element	52.9296	Intensity Mass p 63,549 58,7018 51,9957 50,9415 alculate SFs	(CPS) 298 SF 0.437401 2.97168 0.749563 0.554082 Calcu	117 1sotope ▲ 62.9291 57.935 51.940 50.944 ♥ ▶ ate RSFs
Signal Is Name Cu Ni Cr V Cr V C Add M	otopic Mass 2 Wt 0.2 51.5 16.15 0.22 issing Element	52.9296 * Atomic          -	Intensity Mass p 63.549 58.7018 51.9957 50.9415 alculate SFs	(CPS) 298 0.437401 2.97168 0.749563 0.554082 Calcu	117 62.929 57.935 51.940 50.944 ✓ 0.944 ✓

Following these operations the VAMAS blocks in stainless steel sample is populated with RSFs from the Hastelloy standard. These values can be viewed via the Calibration property page, where the table lists both the RSF per cycle and also the sputter rate per cycle. The remaining step is to assign a sputter rate for the stainless steel sample using the Calibration property page.



#### Specifying the Sputter-Rate

The sputter rate for a profile is updated on the Calibration property page of the Dynamic SIMS dialog window. The information presented on the Calibration property page is designed for calibrating dynamic SIMS profiles. The mechanism allows the specification of sputter rates and RSFs based on matrix materials. Since the RSF is already added to the SNMS data via the Prepare Profiles or SNMS RSF Calculator property pages, the RSF must be retrieved before applying the newly calculated sputter-rate to the SNMS profile. Note that all VAMAS blocks in the row containing the block used to enter the sputter rate are also updated.

To update the sputter rate for a profile, perform the following steps using the Calibration property page.

Calibration       SNMS RSF Calculator       Prepare Profiles         Define Interface       Define Matrix       Ref. Signal       Cr [2]         Define Surf/BG       Matrix In       Interface       RSF       Sputter       C (0)         Dose (atoms/cm2):       Cu (0)       Cu (0)       0.749563       1       1         1.0000e+000       Cu (0)       0.749563       1       1         Depth (nm):        Cu (0)       0.749563       1       1         4.0000e+002       Cu (0)       0.749563       1       1       1         Vol (0)       Cu (0)       0.749563       1	Dynamic SIMS					
Define Interface       Define Matrix       Ref. Signal       Cr [2]         Define Surf/BG       Matrix In       Interface       RSF       Sputter       C (0)         Dose (atoms/cm2):       Cu (0)       Cu (0)       0.749563       1       1         1.0000e+000       Cu (0)       Cu (0)       0.749563       1       1         Depth (nm):        Cu (0)       Cu (0)       0.749563       1       1         4.0000e+002       Cu (0)       Cu (0)       0.749563       1       1       1         V (0)       Cu (0)       0.749563       1	Calibration SNMS RSF	Calculator   F	Prepare Profile	es		
Define Surf/BG       Matrix In Interface       RSF       Sputter       C         Dose (atoms/cm2):       Cu (0)       Cu (0)       0.749563       1       1         1.0000e+000       Cu (0)       0.749563       1       1       1         Depth (nm):       Cu (0)       0.749563       1       1       1         4.0000e+000       Cu (0)       0.749563       1	Define Interface D	efine Matrix	Ref. Signa	I Cr [2]		
Dose (atoms/cm2):       Cu (0)       Cu (0)       0.749563       1         1.0000e+000       Cu (0)       0.749563       1       1         Depth (nm):       Cu (0)       0.749563       1       1         4.0000e+002       Cu (0)       0.749563       1       1         V (0)       Cu (0)       0.749563       1       1         4.0000e+002       Cu (0)       0.749563       1       1         V (0)       Cu (0)       0.749563       1       1         Cu (0)       Cu (0)       0.749563       1       1         V (0)       Cu (0)       0.749563       1       1         U (0)       Cu (0)       0.749563       1       1         U (0)       Cu (0)       0.749563       1       1         U (0)       Cu (0)       0.749563<	Define Surf/BG	Matrix In	Interface	BSE	Sputter	
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Use Ref. Signal       Bulk Doped (atoms/cm3):       1.0000e+000         Compute RSF       Use Bulk Doped       Compute Sputter Rate          RSF:       7.4956e-001       Sputter Rate (cm/s):       5.5003e-005         Apply RSF/SR to Matrix       Apply RSF/SR to Interface       Restore RSF/SR         Depth Profile Calibration       Interface       Normalise to Matrix       Interface Statistics         Calibrate Depth Profile       V Normalise to Matrix       Profile Statistics	Elemental RSF	<		0.749063		>
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Calibrate All Profiles Vise Nano metres Profile Statistics	Calibrate Depth F	Profile	🔽 Normalise	to Matrix	nterface Stat	istics
	Calibrate All Pro	files	🔽 Use Nani	o metres	Profile Statis	tics

- 1. Select an entry from the Matrix Index column as shown.
- 2. Press the RSF button to retrieve the RSF value from the table.
- 3. Enter the Crater depth in the text-field just below the Depth (nm) label before pressing the Compute Sputter Rate button.
- 4. Press the Apply RSF/SR to Matrix button.

#### **Creating a Calibrated SNMS Profile**

Once the set of VAMAS blocks containing the SNMS profile have been populated with RSFs and the sputter-rate, quantification in terms of Atomic or Mass concentrations is achieved by pressing the appropriate buttons on the either the SNMS RSF Calculator property page or the Prepare Profile property page.

Dynamic SIMS	Dynamic SIMS
Calibration SNMS RSF Calculator Prepare Profiles	Calibration   SNMS RSF Calculator   Prepare Profiles
SNMS RSF Calculator Cr Standard © <u>% Weight</u> © % Atomic % 0 Mass per Mole (g) 51.9957 Update Values Signal Isotopic Mass 51.9405 Intensity (CPS) 0	Select Matching Blocks Select and Display Matching Blocks Source VAMAS Blocks Overlaid in the Active Tile Block Id Match String Cr Mass 52
Name     % Wt     % Atomic     Mass p     SF     Isotope       Cr     0     51.9957     1     51.9405              Add Missing Element     Calculate SFs     Calculate RSFs	Copy RSFs to Matching Selected VBs Copy Sputter Rates to All Selected VBs SNMS Quantification Use Nanometres Atomic & by File Mass & by File
SINNS GUARINICADON	Addinic & by rife Index & by rife

These two property pages provide a means of quantifying SNMS data either one file at a time or multiple files in one operation.

The SNMS RSF Calculator property page provides a means of quantifying the SNMS profile in the active tile. To perform the quantification step, display one or more VAMAS blocks in the active tile. Ensure the RSF and sputterrates are correctly assigned for each of the VAMAS blocks by inspecting the table on the Calibration property page. To quantify the profile, press the % Atomic or % Mass buttons on the SNMS RSF Calculator property page. A new experiment frame is created containing a set of VAMAS blocks in which the data are scaled by the sensitivity factors and offered as a percentage of the total scaled intensities. The profiles are therefore presented in the form of an amount of substance rather than the raw signal.

Before quantification the signal is displayed in raw counts against acquisition cycle number.



After quantification, the data are presented in percentage of material against depth in nanometres.

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The alternative to performing the quantification on a file by file basis is to prepare a set of SNMS profiles and then use the Prepare Profile property page to quantify the data in one operation.

Sputter rates may be transferred to other profiles using the Prepare Profile property page in an analogous way to the RSF mechanism.

When multiple VAMAS files are opened in CasaXPS and prepared with appropriate RSF and sputter-rates, the Atomic % by File button or the Mass % by File button may be used to quantify the profiles in each opened file for which at least one VAMAS block is selected and the active tile displays data from one profile in the file. The following steps lead to quantification for two profiles.

1. Tile the experiment frames within the CasaXPS main window

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No.         No	Cu         Mass 53           Ni         Mass 59           Cr         Mass 52           V         Mass 51           Mo         Mass 51           Co         Mass 53           Co         Mass 54           Fe         Mass 54           Fe         Mass 56
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👺 stainless steel set 1 with co.csv.vms	SNMS Quantification
	Use Narometres     Atomic % by File     Mass % by File
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2. Select one of the VAMAS blocks common to both profiles to be quantified and press the Select and Display Matching Blocks button

Select and Display Matching Blocks

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3. Deselect the VAMAS block in the experiment frame for which no quantification is required.

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x 10 <sup>-1</sup> 9 Cu M2 Cr v Mo co w Fe 400 440		
410 0 4 8 12 16 Cycles	Copy RSFs to Matching Selected VBs Copy Sputter Rates to All Selected VBs	
None         Ma	SMMS Quantification V Use Nanometres Atomic % by File Mass % by File	
state of the state		

- 4. Press the Atomic % by File button.
- 5. Review the list of files displayed in the resulting dialog window and press OK if all is well.



Two new experiment frames appear containing the quantified profiles from the two files for which at least one VAMAS block is selected.



Note that:

- Only files in which a VAMAS block is selected are quantified.
- Each raw file contains the information required to perform the quantification and therefore any number of different files can be quantified at once provided the RSF and sputter-rates are prepare appropriately and a selection includes at least one VAMAS block.
- The Control-Key and the mouse can be used to add to the selection across experiment frames, so the operation is not limited by the functionality of the selection options on the Prepare Profile property page.


Hiden SIMS/SNMS Workstation

# **Dynamic SIMS**

The Dynamic SIMS technique etches a sample using an ion gun whilst monitoring the signal for a set of isotopes. The resulting profile represents a measure for the composition of the sample as a function of depth, where raw data takes the form of counts per acquisition cycle as a function of acquisition cycle time. These raw data are calibrated using the tools on the Dynamic SIMS dialog window to provide profiles in terms of atomic density plotted against depth in nanometres.



Quantification of SIMS data is complicated by virtue of measuring the intensity of the secondary ions generated by the interaction of the primary beam on the sample surface. The complexity results from the dependence of the signal intensity on the bulk properties of the sample. That is, a change in the material etched by the ion beam may alter the signal intensity for the secondary ions regardless of the concentration of the element within the surface. It is therefore important to identify the essential structure of a sample, referred to as the *matrix* material, with the understanding that should the matrix material change, both the signal intensity for mass peaks may change as well as possible changes to the etch rate. SIMS analysis is highly sensitive and ideal for the analysis of dopants, diffusion studies and contamination. Quantification schemes for SIMS generally assume that the impurity being measured is dilute (less than a few percent). Above this dilute limit the probability of ionisation becomes dependent upon the impurity concentration itself, as well as the chemistry of the matrix.

# Notes on Dynamic SIMS RSF Calculation

## **Reference Signal Measured during the Course of Profile**

Dynamic SIMS relative sensitivity factors (RSFs) are the means by which measured implant signals are scaled to permit meaningful comparisons of profile data. During the course of a measurement, the signal may change for a variety of reasons and as a result a common practise is to measure both the implant signal and also the matrix signal. The matrix signal provides the experimental context for the implant signal, therefore the calculation of an RSF from a standard sample includes the matrix signal measured in counts per second. Since an RSF is essentially a scale factor and the matrix monitored during the course of the profile is a sequence of measurement, the value included in the RSF calculation is determined from an average of the matrix acquisition cycles.

An alternative to measuring the matrix signal at the same time as the implant is to monitor the matrix signal following the profile completion. The structure of the experiment changes slightly when the matrix signal is determined following the implant measurement, and since the RSF calculation for both scenarios are generalised by the reference signal estimation following the profile, the discussion of the RSF computation will be based on the more general case.

#### **Reference Signal Measured at End of Acquisition Cycles**



Consider a sample created from a matrix material A implanted with a material B using a fluence  $\phi$  atoms per cm<sup>2</sup>. If the resulting sample is profiled using C data acquisition cycles followed by a matrix signal measurement, where each acquisition cycle takes t seconds per cycle and the matrix signal is measured for a further T seconds resulting in a crater of depth d cm, then the RSF for equivalent samples can be determined as follows.

The reference signal measured during the period T corresponding to the etch volume characterized by the depth  $d_2$  is assumed to be representative of the matrix signal throughout the profiled volume characterized by the depth  $d_1$ . Further, the sputter rate is determined from the total depth of the crater equal to  $d_1+d_2$  divided by the total etch time. Hence  $d_1 = td / (t+T)$ . The RSF for the given experiment is:

$$RSF = \varphi \left[ \frac{tCI_A}{I_B - I_{bg}C} \right] \frac{1}{d_1}$$
 (1)

where

- 1.  $I_A$  is the matrix signal in counts per second,
- 2.  $I_B$  is the sum of the signal from the implant over the acquisition cycles

$$I_B = \sum_{i=1}^{C} I_i$$
 in counts,

- 3.  $I_i$  are the counts record for the implant in each cycle and
- 4.  $I_{bg}$  is the background counts for the implant signal.

The formula for the RSF in Equation (1) is defined in terms of parameters determined from an experiment. There are assumptions within this formula regarding the nature of the experiment, which become clear when the parameters are rearranged as follows:

$$RSF = I_A \left[ \frac{\varphi}{d_1 \frac{1}{C} \sum_{i=1}^{C} \left[ \frac{I_i - I_{bg}}{t} \right]} \right]$$
(2)

The denominator in equation (2) is an approximation to the integral of the background subtracted implant counts per second integrated over the depth of the profiled volume. That is:

$$d_{1} \frac{1}{C} \sum_{i=1}^{C} \left[ \frac{I_{i} - I_{bg}}{t} \right] \approx \int_{0}^{d_{1}} \frac{(I(x) - I_{bg})}{t} dx$$
(3)

where the approximation in Equation (1) assumes a uniform step-size  $\Delta x = d_1/C$  for a rectangular integration scheme. If the step-size as a function of depth changes during a calibration profile, the RSF calculated from Equation (1) will be less representative of the measured uncalibrated implant dose. Since the objective of calibrating an implant signal is to ensure that profiles obtained from identical implantation conditions return identical areal densities, or stated mathematically, integrals of the form in (3) for RSF scaled intensities are all the same when calculated from profile data measured for samples with identical implant dose, computation of the integral in Equation (3) is preferable to the summation in the same Equation. Therefore, the RSF calculation in version 2.3.15 of CasaXPS is now performed using:

$$RSF = I_A \begin{bmatrix} \varphi \\ \frac{1}{d_1} \frac{\varphi}{(I(x) - I_{bg})} \\ \int_0^{d_1} \frac{(I(x) - I_{bg})}{t} dx \end{bmatrix}$$
(4)

Equation (4) better represents the nature of the dynamic SIMS RSF as a scaling factor for adjusting implant intensities relative to a known fluence  $\phi$ . The inclusion of the matrix signal  $I_A$  in the RSF calculation is to allow the implant intensity to be further normalised with respect to the matrix signal as a means of removing instrumental variations possible during the course of a profile, or in the case of the reference signal at the end of the profile, between different profile measurements.

## **Quantification of Dynamic SIMS Profiles**

The options on the Calibration property page of the Dynamic SIMS dialog window are designed to permit the analysis of samples for which the matrix material changes in the course of the experiment. Although multilayer materials are analysed using dynamic SIMS, the typical sample consists of a single matrix and one or two impurities appearing in dilute quantities compared to the matrix. For this reason, the first perspective of the Calibration property page will be that of these more common and simple samples.

Most data systems used to acquire dynamic SIMS profiles provide a means of exporting the data in an ASCII format. These data files must be converted to VAMAS format by CasaXPS using a very specific structure within the ISO 14976 definition. The experimental context for the dynamic SIMS profiles is collected into a VAMAS file by CasaXPS and presented as a set of VAMAS blocks. Each VAMAS block within a file manages the quantification information in a set of corresponding variables (as specified by the ISO format). The Calibration property page on the Dynamic SIMS dialog window displays these corresponding variables in a table.



Data file supported by CasaXPS include:

- 1. Hiden Analytical Limited
- 2. Two formats for Cameca IMS instruments.
- 3. RBD Instruments Inc. PHI-upgrade system.

To convert a native ASCII format to VAMAS format suitable for quantification in CasaXPS, convert the data using the Convert option on the File menu or the Convert toolbar option

#### **Quantification of Basic Profiles**

An example based on Cameca IMS-6f old ASCII format.

#### **Converting Cameca Depth Profiles**

Depth profile data from Cameca IMS-6f SIMS instruments can be exported via ASCII formatted files. These files, when written to disk, are assigned a file extension of .dp\_ascii and, if exported from the raw data, include experimental parameters plus two columns of X/Y pairs representing the etch-time per cycle and the secondary ion intensity in counts per second.

SiinGaN_N55C.dp_asci	i - Notepad	
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SII Y	: 0 %	
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Field Aperture	: 750	
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3- DETECTOR PAR	AMETERS	
EM Yield	: 100.0 %	
EM Dead Time	: 25 ns	
EM BackGround	: 0.00E+00 c/s	
FC BackGround	: 2.00E+05 c/s	
EM->FC Threshold	: 8.00E+05 c/s	
FC->EM Threshold	: 1.00E+06 c/s	
ELEMENT 28Si		
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[s] [c/s]	604 T L 05	
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5.889383E+00 2.907	703E+04 243E+04	
0.4023035700 2.238	2425704	~

CasaXPS will convert these .dp\_ascii files only when the raw data is exported. Conversion is performed using the Convert option on the File menu or via the toolbar button. A File dialog window is invoked by these options, in which the .dp\_ascii file containing the raw data is selected and the Open button pressed.

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A new VAMAS file will be written to the same directory containing the original ASCII data after which the profile appears in a new experiment frame in CasaXPS.



When more than one profile is of interest, the data can be combined into a single experiment frame via the Convert and Merge option on the File menu.

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Again a File dialog window appears, in which each .dp\_ascii file within the current directory can be selected using the mouse and the Control Key; on pressing the Open button on the dialog window the entire set of selected dp\_ascii files are converted to VAMAS files and the resulting files loaded into a single experiment frame.



The directory containing the original dp\_ascii files will also contain corresponding VAMAS files. Since the conversion process involves writing new VAMAS files, it is important that the directory containing the data must have write permission and there is sufficient space on the disk to receive the new VAMAS file.

#### Quantification Information

After conversion to VAMAS format, both the timing information and the intensity units are adjusted to those used internally by CasaXPS. Most notably, the intensity unit in the .dp\_ascii file is counts per second, however the intensity in the VAMAS file will be measured in counts per cycle and the abscissa becomes cycle index. All the associated timing information is also save with these abscissa and ordinates so that the calibration to depth and atomic density can be computed later.

Mass channels used to measure the secondary ion intensity are labelled within the .dp\_ascii file using the nominal mass and the element name abbreviation. When entered into the VAMAS file, the block identifier is assigned the original string used to label the mass channel, however CasaXPS attempts to extract the nominal mass and the element abbreviation for use in the element and transition fields used by the VAMAS format. The concatenation of these element and transition fields provides the information used to align the VAMAS blocks within the experiment frame and is also used to determine the isotopic abundance ratio, which in turn is used to determine elemental from isotopic relative sensitivity factors. If the

element/transition fields for a profile are not correctly assigned, should the user request elemental sensitivity factors an error message will result. In the event that the element and transition fields do not contain the element and isotopic information required to determine the relative abundance for an isotope, then these fields must be edited to reflect the true isotope used to measure the profile. To edit these fields:

1. Select the VAMAS block(s) in the right-hand pane of the experiment frame.

2. Press the toolbar button and, on the resulting dialog window, enter the correct element abbreviation and nominal mass for the isotope of those VAMAS blocks in the selection.

When the information on the dialog window is accepted, the VAMAS blocks in the right-hand pane of the experiment frame are re-organised to reflect the new assignment.

One way to check the possible values for the element/transition entries is to use the Exact Mass Calculator property page on the Element Library dialog window.

Element Library			
Element Table Periodic Table	Input File	Exact Mass	
Name	Mass	Time Bin	Rel./
Si28	27.9769	-1	1
Si28			
Add Formula 📃 Define Ti	me <u>3P Cal</u>	ib Calib	) C,t0
Delete Entry Clear Ma	rkers	Find Pe	aks
Delete All 🛛 🗖 Zoom	Create	Load Re	gions
		Create P	eaks
Load Save	Move to Lib	D Ex M	1 T

Enter a string such as "Si28" into the text-edit field on the Exact Mass property page and press return or the Add Formula button. If a valid isotope string has been entered, then the string will be entered into the scrolled list above the text-field. Otherwise, an error dialog indicated an error occurred. If elemental RSF values are desired, it is important the string above the VAMAS block in the experiment frame is accepted by the exact mass calculator; acceptance of a string indicates the database includes the information necessary for the conversion of the RSF.

#### Calculating Relative Sensitivity Factors for Simple SIMS Measurements

Quantification of dynamic SIMS profiles is based on determining absolute scaling factors, which when applied to the profile data convert the raw signal into atom density measured in atoms per cm<sup>3</sup>. Determination of these RSFs requires the measurement of a profile from a material of known composition. For dynamic SIMS, known composition means knowledge of the matrix material and the impurity implant dose used to prepare the standard. The example used to illustrate the process for calculating an RSF is gallium implanted with silicon (dose = 2e14 atoms per cm<sup>2</sup>, crater depth = 1776.4 nm). The profile measured on a Cameca IMS-6f includes the isotopes Ga 69 and Si 28.



The following steps lead to calibrated depth and intensity scales for the data in the original .dp\_ascii file.

- Convert the .dp\_ascii file using the Convert option on the File menu.
- 2. Display the 69Ga data in the active display tile
- 3. Left-click on the active tile to enable the toolbar buttons.



4. Invoke the Dynamic SIMS Calibration dialog window by pressing the



The top left-most text-field displays the Block Id for the data which is the current focus of the Dynamic SIMS dialog window.

Dynamic SIMS toolbar button

Dynamic SIMS		
Calibration SNMS RSF	Calculator   Prepare Profiles	
Define Interface	Define Matrix Ref. Signal 5	9Ga (1)
Dose (atoms/cm2):	Matrix In      Interface      RSF        285i [0]      285i [0]      1        295i [0]      295i [0]      1	Sputter C ^ 1 5
1.0000e+000	2851[0] 2851[0] 1 2851[0] 2851[0] 1 2851[0] 1	1 9
Depth (nm):	285i [0] 285i [0] 1 285i [0] 285i [0] 1 285i [0] 285i [0] 1 285i [0] 285i [0] 1	
Subtract BG	285i [0] 285i [0] 1 285i [0] 285i [0] 1 <	
Use Ref. Signal	Bulk Doped (atoms/cm3): 1.00	000e+000
Compute RSF	Use Bulk Doped Comp	ute Sputter Rate
RSF: 1.0000e+0	00 Sputter Rate (cm/s	s): 1.0000e+000
Apply RSF/SR to Ma	trix Apply RSF/SR to Interface	e Restore RSF/SR
Calibrate Depth	Profile 🛛 🔽 Normalise to Mat	rix Interface Statistics
Calibrate All Pro	files 🔽 Use Nano metres	s Profile Statistics

5. Press the **Define Matrix** button.

Provided no cycles are selected in the scrolled list below the **Define Matrix** button, a dialog window indicates that no selection is active and asks whether all cycles should be updated for the profile in the active tile.

6. Press the **Yes** button and observe that the **Matrix Index** column of the scrolled list is updated with the string 69Ga.

Dynamic SIMS					
Calibration SNMS RSF	Calculator   P	repare Profile	es		1
Define Interface	efine Matrix	Ref. Signa	al   690	ia [1]	
Define Surf/BG	Matrix In	Interface	BSF	Sputter	
Dose (atoms/cm2):	69Ga[1]	28Si [0]	1	1	5
1.0000e+000	69Ga[1]	2851 [U] 285i [O]	1	1	3
Dooth (nm):	69Ga [1]	28Si [0]	1	1	1
	69Ga[1]	285i [0] 285i [0]	1	1	i
1.0000e+007	69Ga[1] 69Ga[1]	28Si [0] 28Si [0]	1	1	1
Subtract BG	69Ga 111	285i î01	1	1	i⊻
Elemental RSF		( ) ( ) ( )			
📃 Use Ref. Signal	вик рореа	(atoms/cm3)	i:  1.000	0e+000	_
Compute RSF	🔲 Use Bul	k Doped	Comput	e Sputter Rate	
RSF: 1.0000e+0	00	Sputter Ral	te (cm/s):	1.0000e+00	0
Apply RSF/SR to Ma	trix Apply	RSF/SR to I	nterface	Restore R	SF/SR
Depth Profile Calibrati	on				
Calibrate Depth	Profile 🛛	Normalise	e to Matrix	Interface St	atistics
Calibrate All Pro	files	🗸 Use Nan	o metres	Profile Sta	tistics

If a cycle selection has been made within the scrolled list, then all cycles must be selected before pressing the **Define Matrix** button is pressed.

The second column in the scrolled list is labelled **Interface**. For this particular profile, the same matrix is present throughout the etch cycles and therefore the use of the Interface column is unnecessary. If the material were a multilayer sample, where RSF and sputter-rates varied between layers, then

the Interface column would need to be populated with strings corresponding to the different materials characterising the layer structure. Once the layers are established, the Interface definition allows the assignment of RSF and sputter-rates to the individual layers.

7. Double-click on the 28Si VAMAS block so that the silicon profile is displayed in the Active Tile.



8. Press the **Define Surf/BG** button.

Two regions are created on the 28Si profile and these mark the surface limit and the background to the secondary ion signal.



Adjustments to these regions are performed using the Quantification Parameters dialog window.

9. On the Calibration property page, enter the crater depth value measured for the standard (crater depth = 1776.4 nm)

Dynamic SIMS					
Calibration SNMS RSF	Calculator   F	Prepare Profil	es		
Define Interface	efine Matrix	Ref. Sign	al 285i	[0]	
Define Surf/BG	Matrix In	Interface	BSF	Sputter	
Dose (atoms/cm2):	69Ga [1]	28Si [0]	1	1	1
1	69Ga[1]	285i [0]	1	i	2
Depth (nm);	69Ga[1] 69Ga[1]	28Si [0] 28Si [0]	1	1	2
1 7764e+003	69Ga[1]	28Si [0] 28Si [0]	1	1	1
Subtract BG	69Ga [1]	285i [0]	1	į	i
Elemental RSF	<	2051101			>
🔲 Use Ref. Signal	Bulk Doped	l (atoms/cm3	0: 1.0000	le+000	_
Compute RSF	🔲 Use Bu	lk Doped	Compute	Sputter Rat	•
RSF: 1		Sputter Ra	ite (cm/s):	1	
Apply RSF/SR to Ma	trix Apply	RSF/SR to	Interface	Restore P	RSF/SR
Depth Profile Calibrati	on				
Calibrate Depth	Profile	Normalis	e to Matrix	Interface S	itatistics
Calibrate All Pro	files	🔽 Use Nar	io metres	Profile St.	atistics

10.Press the Compute Sputter Rate button.

Dynamic SIMS		
Calibration SNMS RSF	Calculator   Prepare Profiles	
Define Interface D	efine Matrix Ref. Signal	28Si [0]
Define Surf/BG	Matrix In Interface RS	SF Sputter C 🔨
Dose (atoms/cm2):	69Ga[1] 28Si[0] 1 69Ga[1] 28Si[0] 1	1 1
1.0000e+000	69Ga [1] 28Si [0] 1	1 2
Depth (nm):	69Ga[1] 28Si[0] 1 69Ga[1] 28Si[0] 1 69Ga[1] 28Si[0] 1	1 2 1 2
1.7764e+003	69Ga[1] 28Si[0] 1	i i
Subtract BG	69Ga[1] 28Si[0] 1 69Ga[1] 28Si[0] 1	1 1
Elemental RSF	<	
🔲 Use Ref. Signal	Bulk Doped (atoms/cm3):	1.0000e+000
Compute RSF	Use Bulk Doped	mpute Sputter Rate
RSF: 1.0000e+0	00 Sputter Rate (c	m/s): 1.8873e-007
Apply RSF/SR to Mat	rix Apply RSF/SR to Inter	ace Restore RSF/SR
Depth Profile Calibratio	n	
Calibrate Depth F	Profile 🔽 Normalise to P	datrix Interface Statistics
Calibrate All Pro	illes 🛛 🔽 Use Nano me	tres Profile Statistics

11.On the Calibration property page, enter the dose value known for the standard (dose = 2e14 atoms per cm<sup>2</sup>)

Dynamic SIMS					_ 🗆 🛛
Calibration SNMS RSF	Calculator   F	repare Profil	es		
Define Interface D	efine Matrix	Ref. Signa	al 285	i [0]	
Define Surf/BG	Matrix In	Interface 28Si I01	RSF 1	Sputter	. <u>c</u> ^
2e14	69Ga[1] 69Ga[1]	285i [0] 285i [0] 285i [0]	1	1	1
Depth (nm):	69Ga[1] 69Ga[1]	285i [0] 285i [0] 285i [0]	1	1	2
Subtract BG	69Ga[1] 69Ga[1] 69Ga[1]	2851 [0] 2851 [0] 2851 [0]	1	1	12~
Elemental RSF	Bulk Doped	(atoms/cm3	1.000	De+000	<u>&gt;</u>
Compute RSF	🔲 Use Bu	lk Doped	Compute	e Sputter Rate	
RSF: 1.0000e+0	00	Sputter Ra	ite (cm/s):	1.8873e-00	7
Apply RSF/SR to Mat	trix Apply	RSF/SR to	Interface	Restore R	SF/SR
Depth Profile Calibration	on			1	
Calibrate Depth F	Profile	Normalis	e to Matrix	Interface St	atistics
Calibrate All Pro	files	🗹 Use Nan	io metres	Profile Stat	tistics

- 12. Press the buttons labelled Compute RSF
  - Dynamic SIMS on SNMS RSF Calculator Prepare Profiles Define Interface Define Matrix Ref. Signal ... 28Si [0] Define Surf/BG 
     Matrix In...
     Interface
     RSF
     Sputter ....
     C ▲

     696a [1]
     285i [0]
     1
     1
     1

     696a [1]
     285i [0]
     1
     1
     1

     696a [1]
     285i [0]
     1
     1
     1

     696a [1]
     285i [0]
     1
     1
     2

     696a [1]
     285i [0]
     1
     1
     2
     Dose (atoms/cm2): 285i [0] 2.0000e+014 Depth (nm): 69Ga [1 69Ga [1 1.7764e+003 Subtract BG Elemental RSF 🗌 Use Ref. Signal Bulk Doped (atoms/cm3): 1.0000e+00 Compute RSF Use Bulk Doped Compute Sputter Rate ... RSF: 1.1236e+020 Sputter Rate (cm/s): 1.8873e-007 Apply RSF/SR to Matrix Apply RSF/SR to Interface Restore RSF/SR Depth Profile Calibration Normalise to Matrix Interface Statistics Calibrate Depth Profile Calibrate All Profiles Vise Nano metres Profile Statistics
- 13.Select one cycle in the scrolled list on the Dynamic SIMS dialog window and press the **Apply RSF/SR to Matrix** button.

Dynamic SIMS		(	
Calibration SNMS RSF Calcul	ator Prepare Profiles	:	
Define Interface Define	Matrix Ref. Signal .	28Si [0]	
Define Surf/BG Mate	rix In Interface	RSF Sputter	. C 🔨
Dose (atoms/cm2): 69G	a [1] 28Si [0]	1 1	1
2.0000e+014 696	285i [0] 285i [0]	1 1	2
Depth (nm): 696. 696.	a [1] 285i [0] a [1] 285i [0] a [1] 285i [0]	1 1 1 1 1 1	2 1
1.7764e+003 69G	a[1] 285i[0] a[1] 285i[0]	1 1 1 1	1
Elemental RSF	a (11 285i (0)	1 1	2
🔲 Use Ref. Signal 🛛 Bulk	Doped (atoms/cm3):	1.0000e+000	
Compute RSF	Use Bulk Doped	Compute Sputter Rate	
RSF: 1.1236e+020	Sputter Rate	(cm/s): 1.8873e-007	7
Apply RSF/SR to Matrix	Apply RSF/SR to Int	terface Restore RS	SF/SR
Depth Profile Calibration			e e 1
Calibrate Depth Profile	Normalise t	o Matrix Interface St.	atistics
Calibrate All Profiles	Use Nano	metres Profile Stat	istics

The values from the two text-fields for the RSF and the sputter-rate will be entered into the corresponding fields in the scrolled-list for each cycle for which the matrix index is identical to the one previously selected.

Dynamic SIMS		
Calibration SNMS RSF	Calculator   Prepare Prol	ïles
Define Interface	Define Matrix Ref. Sign	nal 28Si [0]
Define Surf/BG	Reading to Laboration of	
Dose (atoms/cm2);	69Ga [1] 28Si [0]	1.1236e 1.8873e 1
2.0000e+014	69Ga [1] 28Si [0]	1.1236e 1.8873e 1
2.00000-1014	69Ga [1] 28Si [0]	1.1236e 1.8873e 9
Depth (nm):	69Ga [1] 28Si [0]	1.1236e 1.8873e 6
1.7764e+003	69Ga[1] 28Si[0]	1.1236e 1.8873e 4
Subtract BG	69Ga [1] 28Si [0]	1.1236e 1.8873e 4
Elemental BSE	< 2851101	1.123be 1.8873e 4
Use Ref. Signal	Bulk Doped (atoms/cm	3): 1.0000e+000
Compute RSF	🔲 Use Bulk Doped	Compute Sputter Rate
RSF: 1.1236e+0	20 Sputter R	ate (cm/s): 1.8873e-007
Apply RSF/SR to Ma	trix Apply RSF/SR to	Interface Restore RSF/SR
Depth Profile Calibrati	on	
Calibrate Depth	Profile 🔽 Normali	se to Matrix Interface Statistics
Calibrate All Pro	ofiles 🛛 🔽 Use Na	no metres Profile Statistics

14. Press the button labelled Calibrate Depth Profile.

Dynamic SIMS	
Calibration SNMS RSF	Calculator Prepare Profiles
Define Interface	Define Matrix Ref. Signal 28Si [0]
Define Surf/BG	Matrix In Interface RSF Sputter C
Dose (atoms/cm2):	69Ga[1] 28Si[0] 1.1236e 1.8873e 1 69Ga[1] 28Si[0] 1.1236e 1.8873e 1
2.0000e+014	69Ga[1] 28Si[0] 1.1236e 1.8873e 1
Depth (nm):	69Ga [1] 28Si [0] 1.1236e 1.8873e 6
1.7764e+003	69Ga [1] 285i [0] 1.1236e 1.8873e 4 69Ga [1] 285i [0] 1.1236e 1.8873e 4
🔽 Subtract BG	69Ga [1] 28Si [0] 1.1236e 1.8873e 4 69Ga [1] 28Si [0] 1.1236e 1.8873e 4
🔲 Elemental RSF	
🔲 Use Ref. Signal	Bulk Doped (atoms/cm3): 1.0000e+000
Compute RSF	Use Bulk Doped Compute Sputter Rate
RSF: 1.1236e+0	20 Sputter Rate (cm/s): 1.8873e-007
Apply RSF/SR to Ma	Apply RSF/SR to Interface Restore RSF/SR
Depth Profile Calibrati	on
Calibrate Depth	Profile Normalise to Matrix Interface Statistics
Calibrate All Pro	files Vise Nano metres Profile Statistics

The RSF and sputter-rate entered into the 28Si table are used to compute the atomic density and the depth; the computed profiles are entered into a new experiment frame.



The new experiment frame contains a VAMAS block for each VAMAS block in the original file. Within these new VAMAS blocks, several corresponding variables are defined which are assigned values for the intensity in counts per second plus the RSF and sputter-rate used to calibrate the profile. These values can be viewed using the Crtl PageUp/Crtl PageDown mechanism for stepping through the corresponding variables in a VAMAS block.

NB: To compute the elemental RSF from an isotope profile, the tick-box labelled **Elemental RSF** must be ticked and the element/transition field for the VAMAS block in use must be set appropriately.

## Making Adjustments to the Sputter Rate

A depth profile prepared for calibration must have an RSF and sputter rate defined for each matrix within the analysis volume. If at a later time it is desired to alter the RSF or sputter rate for a given matrix, the following sequence of steps should be used:

- 1. Select a cycle from the scrolled-list to identify the matrix for which the RSF or sputter-rate requires adjusting.
- 2. Press the pushbutton labelled Restore RSF/SR.

Dynamic SIMS				
Calibration SNMS RSF Calculator Prepare Profiles				
Define Interface	efine Matrix Ref. Signa	al 285i [0]		
Define Surf/BG	Matrix In Interface	RSF Sputter CA		
Dose (atoms/cm2):	69Ga [1] 28Si [0]	1.1236e 1.8873e 1		
2.0000e+014	69Ga [1] 28Si [0]	1.1236e 1.8873e 1		
Depth (nm):	69Ga (1) 28Si (0) 69Ga (1) 28Si (0) 69Ga (1) 28Si (0)	1.1236e 1.8873e 9 1.1236e 1.8873e 6 1.1236e 1.8873e 4		
1.7764e+003	69Ga [1] 28Si [0]	1.1236e 1.8873e 4		
🔽 Subtract BG	69Ga[1] 28Si[0] 69Ga[1] 28Si[0]	1.1236e 1.8873e 4		
Elemental RSF	<	>		
🔲 Use Ref. Signal	Bulk Doped (atoms/cm3)	1.0000e+000		
Compute RSF	🔲 Use Bulk Doped	Compute Sputter Rate		
RSF: 1.1236e+0	20 Sputter Rat	re (cm/s): 1.8873e-007		
Apply RSF/SR to Mat	trix Apply RSF/SR to I	nterface Restore RSF/SR		
Depth Profile Calibration				
Calibrate Depth F	Profile 🔽 Normalise	e to Matrix Interface Statistics		
Calibrate All Pro	files 🔽 Use Nand	o metres Profile Statistics		

The values for the matrix identified by the chosen cycle are entered into the corresponding text-fields for the **RSF** and **Sputter Rate** on the dialog window.

 Either the RSF, the sputter rate or both the RSF and the sputter rate can be recalculated before again pressing the Apply RSF/SR to Matrix button. The matrix defined by the selected cycle will be updated with the modified values.

#### **Display of Calibrated Profiles**

The labels for identifying the x and y axes in a display tile are determined from the first VAMAS block with respect to the order of selection in the righthand pane of the experiment frame at the time the VAMAS blocks are overlaid in the display tile. If a row of VAMAS blocks are selected by clicking on the experimental-variable value for the row, then the left-most VAMAS block will determine the axes labels. Matrix signals are typically not calibrated and in the event the first VAMAS block contains the matrix signal, the profile would appear with the y-axis displaying an arbitrary scale.

69Ga



When calibration is performed, only those profiles for which quantification information is supplied are converted to atom density. Profiles with an RSF of unity are scaled to ensure the profiles appear within the range for the calibrated profiles; hence the y-axis label is assigned the string "Arbitrary Units". To display an overlay of the profiles where the Y axis is labelled with respect to a calibrated profile, namely "Atomic Density", it is necessary that a calibrated VAMAS block is selected first. To select VAMAS block in an arbitrary order, left-click the first VAMAS block, then hold the Control Key down and left click the other blocks required for the display. The traces are displayed in the active tile by pressing the overlay toolbar button to the selection sequence.



The VAMAS block for the impurity 28Si is selected before the matrix 69Ga.

## Further Aspects of Dynamic SIMS Quantification

#### Logical Structure of a SIMS Depth Profile within CasaXPS

A depth profile is a collection of VAMAS block all assigned to the same experimental variable value; typically the experimental variable will be an index number for a given file of data. There may be more than one profile per VAMAS file, where each profile will occupy a row as viewed via the right hand pane of the experiment frame.



For each VAMAS block within a raw depth profile, a number of corresponding variables are setup to offer fields for use in the quantification step. The important fields for quantification are displayed in the Matrix Index table on the Calibration property page of the Dynamic SIMS dialog window.

Dynamic SIMS					
Calibration SNMS RSF Calculator Prepare Profiles					
Define Interface   Define Matrix   Ref. Signal   FSi [2]					
Define Surf/BG	Matrix In	Interface	RSF	Sputter C 🔨	
Dose (atoms/cm2):	Si [3] Si [3]	FSi [0] FSi [0]	2.0675e 2.0675e	1.4305e 1	
2.0000e+014	Si [3]	FSi [0]	2.0675e	1.4305e 9	
Depth (nm):	Si [3]	FSi [0]	2.0675e	1.4305e 1	
1.7150e+003	Si [3]	FSI [0]	2.0675e 2.0675e	1.4305e 1 1.4305e 2	
🔽 Subtract BG	Si [3] Si [3]	FSi [0] FSi [0]	2.0675e 2.0675e	1.4305e 2	
Elemental RSF	Elemental RSF				
Use Ref. Signal			•  1.0000e+	000	
Compute RSF	Compute RSF J Use Bulk Doped Compute Sputter Rate				
RSF: 2.2963e+0	RSF:      2.2963e+021      Sputter Rate (cm/s):      1.3972e-007				
Apply RSF/SR to Matrix Apply RSF/SR to Interface Restore RSF/SR					
Depth Profile Calibration					
Calibrate Depth Profile Viormalise to Matrix					
Use Nano metres Profile Statistics					

## Methods for Computation of RSF and Sputter Rate Values

RSF values are computed from standard materials using one of three approaches:

- 1. Matrix, dopant and crater depth.
- 2. Matrix, known bulk doped atomic density and crater depth.
- 3. Interface assignment with respect to depth and atomic density.

The computation of the RSF requires the determination of values from the Matrix signal and also the Implant. To support the determination of these quantities the matrices within a profile must be identified and a pair of regions defined to specify the surface zone as well as the appropriate background signal for a given mass.

## Identification of the Matrix and Interface Cycles

Defining the matrix for experiments involving a **Single matrix material** is achieved as follows:

- 1. Display the matrix signal for each profile in the active display tile.
- 2. Press the Define Matrix button on the Calibration property page on the Dynamic SIMS dialog window.

A pop-up window will inform you that no matrix index is selected and asks whether the displayed matrix should be applied to all Cycles. Answer by pressing the Yes button. To avoid the warning message, before pressing the Define Matrix push button, first select all the table entries by pressing the header button for the column labelled Matrix Index. If there are any rows currently selected it will be necessary to de-select these rows before pressing the header Matrix Index.

If the file contains more than one depth profile and the matrix for each profile is overlaid in the active tile, then the operation of defining the matrix for each depth profile is performed in one go.

Defining the matrix for **Layered materials** is achieved as follows:

A key point for SIMS is that the signal from a given mass peak depends on the environment in which the isotope is found. As the crater bottom moves through an interface between differing materials there is potential for both the relative sensitivity and the etch rate to change during the course of the acquisition. The example used to illustrate a layered material involves profiling magnesium in gallium with an aluminium layer in the form of GaN : AlGaN : GaN (Dr Shadi Shahedipour, University of Albany, New York).



The secondary ion yield for Mg differs between the GaN and the AlGaN layers. Presentation of these types of samples requires a means of adjusting the Mg RSF for acquisition cycles depending on the aluminium signal strength.

The table on the Calibration property page provides two columns headed Matrix Index and Interface. These columns specify the matrix material and also structures within the profile where the RSFs for a given isotope change due the material environment rather than changes to the atomic density. The procedures for defining the matrix and also a layer are identical except for different buttons are used to make the assignment. For the current example, the Ga<sub>2</sub> signal is most representative of the gallium matrix, while the Al signal best defines the interface between the GaN and AlGaN layers. The matrix signal Ga<sub>2</sub> is common to both layers therefore the Ga<sub>2</sub> profile can be defined as the matrix throughout the profile:

1. Display the Ga<sub>2</sub> VAMAS block in the active tile.



2. Ensure the Matrix Index column of the table on the Calibration property page is either all selected or none are selected before pressing the Define Matrix button.

Dynamic SIMS				
Calibration SNMS RSF	Calculator P	repare Profi	les	
Define Interface	Define Matrix	Ref. Sign	al   Ga2 [2]	
Define Surf/BG	Matrix In	Interface	RSF	Sputter 🔨
Dose (atoms/cm2):	Ga2 [2] Ga2 [2]	69Ga [0] 69Ga [0]	1	1
1.0000e+015	Ga2 [2]	69Ga [0]	1	1
Depth (nm):	Ga2 [2]	69Ga [0]	1	1
4.7804e+002	Ga2 [2] Ga2 [2]	69Ga [0] 69Ga [0]	1	1
Subtract BG	Ga2 [2] Ga2 [2]	69Ga (0) 69Ga (0)	1	1 💌
Elemental RSF				
Use Ref. Signal	Bulk Doped	(atoms/cma	9:  1.0000e+	-000
Compute RSF	Use Bu	k Doped	Compute S	putter Rate
RSF: 8.2407e+0	20	Sputter Ra	ite (cm/s):	3.6631e-008
Apply RSF/SR to Matrix Apply RSF/SR to Interface Restore RSF/SR				
Depth Profile Calibration				
Calibrate Depth Profile Vormalise to Matrix Interface Statistics				
Calibrate All Pro	ofiles	🗸 Use Nar	io metres	Profile Statistics

All VAMAS blocks from the same row in the right-hand pane will now show the same Ga2[2] matrix for each cycle throughout the profile.

At this point the Interface column is populated with the 69Ga[0] reference, that is, the matrix and interface columns are initialised to the first VAMAS block in the file. Only the matrix has so far been replaced by a reference to the Ga2[2] VAMAS block. Since the depth profile includes two environments from which the Mg signal is measured, to distinguish between these two environments the cycles corresponding to the AlGaN layer must be identified. The Al signal provides the means of specifying the appropriate set of cycles for which AlGaN is significant compared to the GaN layers.

1. Display the signal for Al in the active display tile.



2. Either using the table or the mouse (see below), select ranges of cycles within the Matrix Index column of the table on the Calibration property page.



3. Press the Define Interface button. Only those cycles selected in the table will be assigned the VAMAS block reference Al[1].



#### Selecting Ranges of Cycles on the Calibration Property Page

Selecting rows within the Matrix Index table is achieved using the table together with the Shift and Control Keys. Alternatively, the selection can be defined using the active tile and the mouse. When the Shift Key is held down and the left mouse button is used to drag over the display, the set of cycles corresponding to those lying between the vertical cursors will be selected in the Matrix Index table.



The use of the cursor and Shift key aids the identification of layered structures viewed via a profile signal. Once a set of layers are so indicated, the assignment is made by pressing the Define Matrix or Define Interface button, as appropriate.

## Surface Data and Background Signal

Since SIMS signal intensity depends on the matrix material, adventitious carbon or other surface contaminants may result in signal from the surface deviating from the bulk behaviour. It is therefore sometime appropriate to exclude surface acquisition cycles from the RSF determination. Further a bulk material may also cause a residual signal for the implant and therefore removal of a background count rate is also appropriate. To aid the specification of these two limitations when calculating RSF values, two regions must me defined for each VAMAS block before an RSF can be computed.

Defining the Surface and Background Regions:

- 1. Display any number of VAMAS blocks in the active display tile.
- 2. Press the Define Surf/BG button.

Dynamic SIMS				
Calibration SNMS RSF	Calculator   F	Prepare Profil	es	
Define Interface	Define Matrix	Ref. Signa	al   Al [1]	
Define Surf/BG	Matrix In	Interface	RSF	Sputter 🔨
Dose (atoms/cm2):	Ga2 [2]	AI [1]	1	1
1.0000e+015	Ga2 [2] Ga2 [2]	AI [1] AI [1]	1	1
	Ga2 [2]		1	1

Two regions will appear on each profile; the left most region indicates the peak and should be adjusted to start just after cycles associated with any surface spike. The second right-most region defines the background to the tail of an implant. Both regions can be adjusted using the Quantification Parameters dialog window when viewing the Regions property page. The left mouse button may be used to drag the start and end position of these regions whenever the Region property page is active. Adjustment under mouse control is available when grey vertical lines at either end of the regions are displayed which appear when the Region property page is top-most on the dialog window.



## Three Ways to Calculate RSF Values from Standard Samples

Once the matrix and regions have been defined, the RSF can be computed by the appropriate method:

- Either: enter the Implant dose in Atoms/cm<sup>2</sup> and the measured crater depth in nanometres then press the Compute Sputter Rate button before pressing the Compute RSF button. Pressing these buttons will result in the corresponding values appearing in the boxes below the buttons.
- Alternatively, if a bulk doped standard is in use, tick the box labelled
  Use Bulk Doped and enter the known atom density into the above data input field. When a bulk doped standard is used to compute the RSF, both the implant and matrix require regions.
- The third method for computing the RSF is via a known implant depth and atom density. The button to the right of the Depth field, namely, Depth (rm): \_\_\_\_\_ results in a dialog window in which a depth and/or a peak intensity can be entered. The position of the implant is defined using the Matrix Index table by making a single selection in that table. The appropriate cycle can be identified by left-clicking on the peak in the left-hand pane active tile. The Matrix Index table scrolls to show the cycle corresponding to the mouse selection and the table entry is

therefore offered for selection prior to invoking the Define Depth by Cycle dialog window. If the correct depth and corresponding atoms per cm<sup>3</sup> are entered, the Calc RSF tick box is ticked and the OK button is pressed, the RSF, Depth and Sputter Rate fields will be updated.

Define Depth by Cycle		
299	OK	
1000000	Cancel	
1	🗖 Calc RSF	
	y Cycle 299 10000000 1	

#### Adding RSF and Sputter Rates to Profile Data

Once an RSF is computed and the appropriate Sputter Rate entered for an implant in a given matrix, the profile can be update with these values: select a cycle from the Matrix Index table with the appropriate matrix entry and

press either the Apply RSF/SR to Matrix button or the Apply RSF/SR to Interface button. Each cycle within the profile with the same entry as the selected matrix index will be updated with both the Sputter Rate and the RSF. If the material is a multilayer structure the procedure should be repeated for each layer, where the RSF and Sputter Rates are first determined from a standard profile. An RSF/Sputter Rate pair can be extracted from another profile by first displaying the profile, making a selection in the Matrix Index table and

pressing the Restore RSF/SR button. The RSF/Sputter Rate from the indicated matrix index will be entered into the fields on the dialog window, thus allowing the unknown to be subsequently displayed and these restored values from the standard used to update the unknown profile. Note, the Dose and depth for single matrix material are computed when the button **Apply to Selected Matrix** is pressed.

#### Applying Calibration Parameters to One or More Profiles

Once RSF and Sputter Rates have been assigned to each depth profile, the data are calibrated by pressing the Calibrate Depth Profile button. If multiple profiles are prepared and overlaid in the active tile, pressing the Calibrate All Profiles button results in each profile, so selected, being calibrated and

entered into a single experiment frame. The depth scale units must be selected prior to calibration using the tick box **Use Nanometres**.

Note: If normalization to the matrix is not requires, it is necessary to compute the RSF with the same selection of the Normalize tick box.



## Depth Profile Statistics: Areal Density and Decay Length

Areal Density and Decay Length are computed as part of the Depth Profile Statistics. The procedure for calculating these statistics requires a pair of cursors to be defined on the displayed profile in the active tile. The aim is to mark the region over which the profile peak appears. To mark the cursors on the profile: hold the Shift Key down and drag a box starting from the left of the peak and ending at the right-hand end with the mouse positioned at the intensity of the background. On pressing the Profile Statistics button a dialog window appears showing the current text in the VAMAS block comment plus a set of lines offering the new calculated profile statistics. If it is desired to include these new lines in the VAMAS block comment, then the OK button should be pressed, otherwise the Cancel button will exit without altering the VAMAS block comment. Note, the text in the VAMAS block comment can be edited within this window leaving only the information so required.



## **Maintaining Standards Library Files**

Once standards have been prepared and RSF/Sputter Rates computed, these depth profiles can be moved to other files containing profiles from standards.

The toolbar buttons is allow VAMAS blocks to be copied into an existing file and also delete from a file. If a number of standard material

profiles are located in a single file, the button offers a means of searching the strings within a VAMAS block comment and those matched are both selected in the right-hand pane of the experiment frame and are also displayed in the scrolled list of display tiles. VAMAS block comments can be edited using the toolbar button.

# Step-by-Step Description of Quantification for a Multi-Layer Sample

In this example, the desired result is to plot atomic density verses depth for Mg implanted in Gallium. To achieve this end and owing to the layered structure, four masses were monitored, where two labelled 69Ga and Al define the layer structure while the trace labelled Ga<sub>2</sub> represents a constant matrix signal, to which the Mg signal is normalized.



#### Step 1: Define the Matrix

Display the matrix VAMAS block, namely, Ga2 in the activetTile. The block id plus the VAMAS Block index for the trace will appear on the Calibration property page of the Dynamic SIMS dialog window.



Select all the cycles under the Matrix Index column in the table on the Calibration property page and press the Define Matrix button; the selected entries under the Matrix Index column will change to Ga2[2], thereby showing the matrix is defined.

#### Step 2: Define the Layer Structure

The structure of the material is GaN : AlGaN : GaN (Dr Shadi Shahedipour, University of Albany, New York) therefore the matrix definition alone is not sufficient to specify the cycles for which different sputter rates and RSF must be assigned. Thus a sample such as this one requires the definition of quantification information using the interface column within the table on the Calibration property page. The AlGaN layer is characterized by the trace labelled Al. To define a layer within the profile, the signal Al is used to select the set of cycles recorded between the two interfaces.



Before using the mouse to indicate the interfaces, ensure there are no selected cycles in the table on the Calibration property page. Clicking on any column away from the Matrix Index column will de-select all cycles. Note, repeated use of the mouse will add to the current selection, allowing complex multilayer materials to be specified. Mark the AlGaN layer by holding the Shift-Key down and then dragging a box from the left to the right of the AlGaN peak. The result of such an action is shown in above. All the cycles within the table on the Calibration property page between the vertical cursors shown above are selected by the mouse action and so pressing the **Define Interface** button on the same property page will cause the Interface column in the table to be updated.

Dynamic SIMS					
Calibration SNMS RSF Calculator Prepare Profiles					
Define Interface D	efine Matrix Matrix In	Ref. Signa	al Al [1	]	
Dose (atoms/cm2):	Ga2 [2] Ga2 [2] Ga2 [2]	69Ga [0] 69Ga [0] Al [1]	1 1	1 1 1	1 3
Depth (nm):	Ga2 [2] Ga2 [2] Ga2 [2] Ga2 [2]	AI [1] AI [1] AI [1] AI [1]	1 1 1 1	1 1 1 1	3 1 4 8
✓ Subtract BG	Ga2 [2] Ga2 [2] <	AI [1] AI [1]	1	1	1 1 ¥
🔲 Use Ref. Signal	Bulk Dope	d (atoms/cm3	): 1.0000	)e+000	
Compute RSF	🔲 Use B	ulk Doped	Compute	Sputter Rate	
RSF: 1.0000e+00	00	Sputter Ra	te (cm/s):	1.0000e+0	00
Apply RSF/SR to Mat	rix Appl	y RSF/SR to I	Interface	Restore R	SF/SR
Depth Profile Calibratic Calibrate Depth F	n Profile	Vormalise	e to Matrix	Interface S	tatistics
Calibrate All Prot	files	🔽 Use Nan	o metres	Profile Sta	itistics

#### Step 3: Enter RSF and Sputter Rate Values

In this example the RSF and Sputter Rate for the two layers are assumed to be known. All that is required is to add sputter rates and RSF for each of the three layers; the values are entered on the Calibration property page. The required information for quantification are two RSF and SR pairs, which must be entered correspondingly for the GaN and AlGaN layers. Since the matrix does not define the layer structure, the assignments are made by using the **Apply RSF/SR to Interface** button. After displaying the Mg trace in the active tile the RSF and sputter rate for each layer can be entered in turn. Since the Interface column was initially all assigned 69Ga[0], the layer assignment based on the Al signal only altered the range of cycles specified by the vertical cursors. As a result the GaN layers are assigned RSF and sputter rates by selecting one cycle for which the interface column contains 69Ga[0], entering the appropriate RSF/SR and pressing the **Apply RSF/SR to Interface**.

button. Each cycle previously designated as part of the 69G [0] layer will receive the RSF/SR pair.

Dynamic SIMS			×	
Calibration SNMS RSF Calculat	or Prepare Profiles	1		
Define Interface Define M Define Surf/BG Dose (atoms/cm2):	atrix Ref. Signal	Mg [3] RSF Sputter C 8 2665e 3 6631e 3		
1.0000e+015	<b>69Ga[0]</b> 8 <del>83Ga[0]</del> 8	8.2665e 3.6631e 2 — 8.2665e 3.6631e 2		
Ga2 [2 Depth (nm): Ga2 [2 4.7804e+002 Ga2 [2	1] 69Ga(0) 8 1] 69Ga(0) 8 1] Al(1] 1 1] Al(1] 1	8.2665e 3.6631e 2 8.2665e 3.6631e 1 1 1 1 1 1 1		
Ga2 [2 Ga2 [2 Ga2 [2 Ga2 [2				
Use Ref. Signal Bulk D	oped (atoms/cm3):	1.0000e+000		
Compute RSF	se Bulk Doped	Compute Sputter Rate		
RSF: 8.2665e+020	Sputter Rate	(cm/s): 3.6631e-008	]	
Apply RSF/SR to Matrix	Apply RSF/SR to Inte	terface Restore RSF/SR		
Depth Profile Calibration				
Calibrate Depth Profile	🗌 🔽 Normalise to	o Matrix Interface Statistics		
Calibrate All Profiles	📃 🔽 Use Nano n	metres Profile Statistics		

Similarly, the AlGaN RSF/SR values are entered in the text-fields, one cycle with an Interface column of Al[1] selected and the **Apply RSF/SR to Interface** button pressed a second time. Again, each cycle designated as Interface Al[1] will receive the RSF/SR pair.

Dynamic SIMS				
Calibration SNMS RSF Calculator Prepare Profiles				
Define Interface	efine Matrix Ref. Signal Mg	[3]		
Define Surf/BG	Matrix In Interface BSE	Soutter CA		
Dose (atoms/cm2):	Ga2 [2] 69Ga [0] 8.2665e Ga2 [2] 69Ga [0] 8.2665e	a 3.6631e 3		
1.0000e+015	Ga2 [2] 63Ga [0] 6.26656 Ga2 [2] 69Ga [0] 8.26656 Ga2 [2] 69Ga [0] 8.26656	a 3.6631e 2 2.6631e 2		
Depth (nm):	Ga2 [2] 69Ga [0] 8.26656 Ga2 [2] 69Ga [0] 8.26656	a 3.6631e 1		
4.7804e+002	Ga2[2] Al[1] 6.36e+0 Ga2[2] Al[1] 6.36e+0 6.36e+0 6.36e+0	) 4e-008 1 ) 4e-008 1		
Subtract BG	Ga2 [2] Al [1] 6.366+0	) 4e-008 3 ⊻		
Elemental HSF	Bulk Doped (atoms/cm3): 1 000	0e+000		
Compute RSF	Use Bulk Doped Compute	e Sputter Rate		
RSF: 6.3600e+0	20 Sputter Rate (cm/s):	4.0000e-008		
Apply RSF/SR to Ma	trix Apply RSF/SR to Interface	Restore RSF/SR		
Depth Profile Calibration				
Calibrate Depth I	Profile Normalise to Matrix	Interrace Statistics		
Calibrate All Pro	files 🔽 Use Nano metres	Profile Statistics		

#### Step 4: Calibrate Mg Profile

Calibration is performed by displaying the Mg profile in the active tile and pressing the Calibrate Depth Profile button.



In this example, the only mass for which RSF/SR pairs are entered is Mg. The SR are automatically assigned to all masses, however the RSF values for masses other than Mg remain set equal to unity. A consequence of leaving an RSF equal to unity is that on Calibration to atomic density and depth, masses for which the RSF is equal to unity will be scaled to the atomic density range of any properly calibrated masses. This allows an overlay with respect to the calibrated traces, without requiring the RSF for all masses to be assigned prior to calibration. Counts per second traces are available in the calibrated experiment frame as the second corresponding variable (Ctrl PageUp/Crtl Page Down).



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# An Example of Computing an RSF using Dose and Implant Peak Depth

A profile was obtained from GaN undoped epi growth ion implanted with <sup>24</sup>Mg at a dose of 1.0e15 atoms per cm<sup>2</sup>. The depth at the peak of the Mg counts is 77 nm. Computation of an appropriate RSF is performed as follows:



## Step 1: Define the Matrix

Display the Ga2 matrix profile in the Active Tile, press the header button labeled Matrix Index in the table to select all cycles and press the Define Matrix push button on the Calibration property page. The table on the same property page will update to show that the Matrix index for each cycle is now assigned to the Ga2 profile.

## Step 2: Define the Surface Layers and also the Background for the Mg Profile

Display the Mg profile in the active tile and press the button labeled Define Surf/BG. Two regions are created on the Mg profile. The left-most end of the left-most region defines the surface layers, while the background to the right-most of the two regions estimates the background to the Mg signal.

#### Step 3: Define the Depth Scale

In this example, the depth scale is defined to be 77nm at the maximum signal for the Mg profile. Using the left-mouse button, click on the profile to indicate the position of the Mg maximum values. The table entries on the Calibration property page will scroll so that the cycle corresponding to the position of the vertical cursor, which is located at the top of the visible portion of the list. Select the entry at the top of the visible portion and press the button next to the Depth (nm): label. A dialog window appears in which the selected cycle index in already entered and a text-field for the Depth (nm) corresponding to the indicated cycle can be input.



On pressing the OK button, the Calibration property page is updated with the depth computed from the **Define Depth by Cycle** dialog window values.

## Step 4: Enter the Dose and Compute the RSF

Enter the dose in atoms per cm<sup>2</sup> on the Calibration property page and press the button labelled **Compute RSF**. If the elemental RSF is required, the tickbox just above the Compute RSF button should be ticked.

#### Step 5: Calibrate the Mg Profile

Once the RSF is computed and the sputter rate updated, the values for each cycle corresponding to the Mg profile (currently displayed in the active tile) must be updated. In this example, the assignment for the matrix is sufficient to target the cycles for which RSF and sputter rates must be applied. Simply select any cycle using the Matrix Index column in the table and press the **Apply RSF/SR to Matrix** button. Since all the cycles are defined to have the same matrix, the table for the Mg profile will contain values for the RSF and sputter rate throughout. To calibrate the profile, press the button labelled **Calibrate Profile**.
Standard GaN Matrix Mg Implant Areal Density 1.038e+015 atoms/cm2, Background Intensity = 3.782e+017 atoms/cm3 Peak Height 1.113e+020 atoms/cm3, Peak depth 76.598 nm Decay Length (11e),45.661 nm (110):105.14 nm



Note that the Profile Statistics button has been used to create a VAMAS block comment showing the Areal Density and Decay Length for the Mg profile. Also note how the profiles for which no RSF is specified are scaled to allow their visualization within the same scale as the calibrated Mg profile.



## Computing RSFs where the Matrix Signal is Measured following the Completion of the Implant Profile

Cameca dynamic SIMS instruments permit experiments in which only the implant is profiled. The inclusion of the matrix intensity in the computed RSF is achieved by measuring the matrix signal after the implant signal attenuates

to background levels. The assumption is therefore that the matrix count rate is constant during the acquisition of the dopant profile. While in principle the Cameca files contain the experimental parameters for the profile, there are occasions where the matrix reference signal must be inspected and manually entered. To calculate the RSF for a standard material based on an implant profile only, the following features are employed.

The VAMAS file for a single boron implant in silicon consists of a single VAMAS block.



Following the measurement of the boron profile, the Cameca monitors the matrix signal, and records the counts per second for the matrix in the data file. It should be noted that the crater depth measured following such an experiment includes the depth etched during the matrix measurement which occurs after the boron profile is completed.

Calculation of the RSf for <sup>11</sup>B implanted in silicon is computed identically to previous examples with the exception that the user inputs the matrix signal in counts per second via the Ref Signal button on the Calibration property page. The VAMAS block containing the boron profile is updated with the intensity of the matrix signal via the Reference Signal dialog window invoked by the Ref Signal button.

Dynamic SIMS		
Calibration SNMS RSF 0	Calculator Prepare Profiles	
Define Interface D	efine Matrix Ref. Signal 11B [0]	
Define Surf/BG	Matrix In Interface BSE Souther CA	
Dose (atoms/cm2):	Reference Signal	
5.0000e+014		
Depth (nm):	Cancel	
7.7000e+002		
💌 Subtract BG	Reference Signal CPS: 277800000	
Elemental RSF	, i i i i i i i i i i i i i i i i i i i	
🔽 Use Ref. Signal		
Compute RSF	Use Bulk Doped Compute Sputter Rate	
RSF: 7.3204e+022 Sputter Rate (cm/s): 1.9593e-007		

Computing the RSF is performed as follows:

- 1. Enter the crater depth (770 nm) and press the Compute Sputter Rate button.
- 2. Enter the dose  $(5x10^{14} \text{ atoms per cm}^2)$ .
- 3. Check that the reference signal is correctly assigned and enter the correct value by pressing the Ref Signal button.
- 4. Press the Compute RSF button.

## Gathering Profile Data for Display and Calibration Purposes

Profile data typically is stored as individual VAMAS files. There are however reasons why merging these files into a single experiment frame is desirable. For example, data can only be overlaid for display purposes for data located in the same experiment frame. A further reason for moving profiles into a single experiment frame is that Calibration of a dynamic SIMS profile is performed on the Calibration property page and the button for calibrating multiple profiles only acts on data within a given experiment frame. Copying profiles into a single experiment frame permits many profiles to be calibrated in one action.

By way of example, consider merging two VAMAS files containing profile data for which a display of the data in overlay format is required.

- 1. Open each of the two data files in CasaXPS.
- Using the Window menu, tile the two experiment frames so that both right-hand panes are visible such that the VAMAS blocks are easily selected.



3. Create a new experiment frame and press the Copy/Paste VAMAS blocks toolbar button.

🔓 CasaXPS Licensed to:A1 CASA - [CasaXP5]	×
📴 File View Window Options Select Help 🔤	5 ×
	T I
M 林戸原身家 這 時 計像 五面画 图标色版 《 《月本》 杜云 图 副 王	
····································	
	_
Copy Selected VAMAS Blocks	
Increment Exp Variable Cancel	
Selected Block Id. File Name	
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Mass2 rrs1Ub.dat hies1Ub-1U9.vms: c:\documents and settings\nealking documents\working	
Massi Irisi U/. dat riesi Uo-109 vms; c. \addcuments and settings\neal\my documents\workir	
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Mass1 rrsf102.dat file102-105.vms : c:\documents and settings\neal\my/documents\working	
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4. Check that the VAMAS blocks listed on the Copy Selection dialog window match those selected in the two files and press the OK button.

The selected VAMAS blocks now appear in the new experiment frame. Note that the selected VAMAS blocks are transferred to the experiment frame with focus. In the event that the experiment frame with focus already contains VAMAS blocks the selected VAMAS blocks are appended to the existing blocks. The target experiment frame for this example was initially empty therefore only the selected blocks appear in the experiment frame.



5. Save the new experiment frame to disk.

After preparing the profiles with appropriate RSFs and sputter rates the entire set of profiles is calibrated by overlaying the implant VAMAS blocks in the active tile and pressing the Calibration All Profile button.



## A new experiment frame appears contain the quantified profiles.

