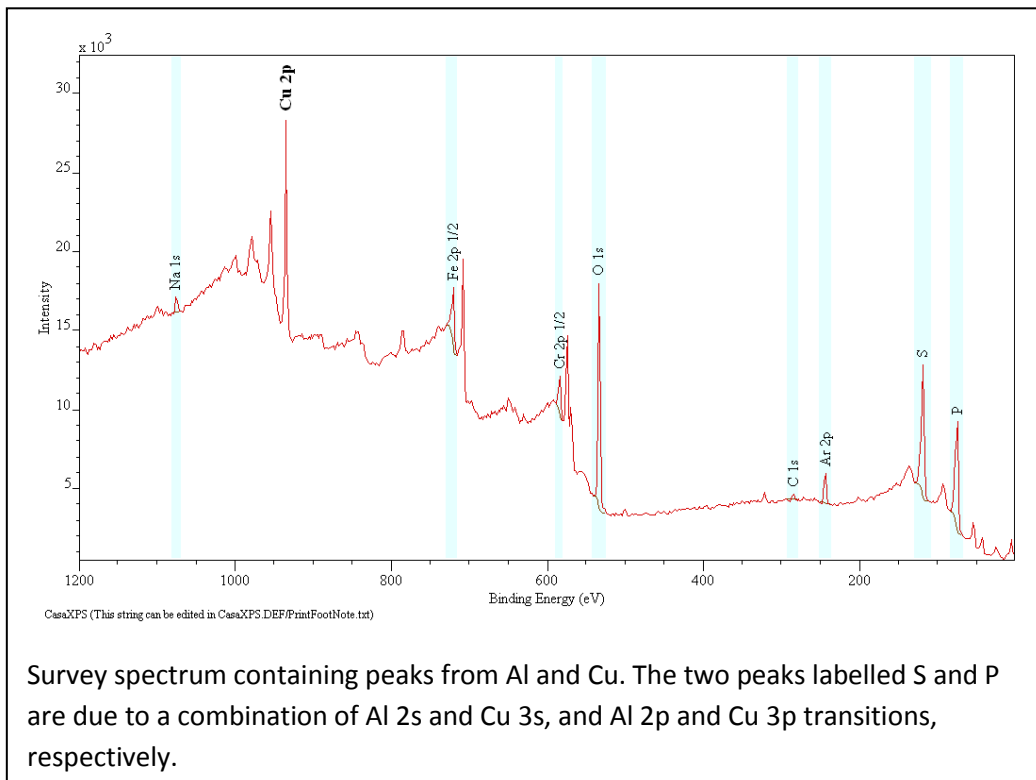# Custom Report: XPS Spectra containing Copper and Aluminium

Measuring aluminium using XPS survey spectra when copper is present in the sample is an issue because the two aluminium peaks available for quantification of the aluminium signal, namely Al 2p and Al 2s, overlap with the Cu 3p and Cu 3s peak positions. While at first sight the need for high resolution spectra from the Al 2p region might seem the only solution the problem can be addressed via survey spectra using the ideas described by Hazell SIA (2002). Apart from solving the problem for materials with both Al and Cu, the solution illustrates how the custom report in CasaXPS can be used to manipulate peak intensities leading to an indirect quantification for a sample.



Survey spectrum containing peaks from Al and Cu. The two peaks labelled S and P are due to a combination of Al 2s and Cu 3s, and Al 2p and Cu 3p transitions, respectively.

Direct quantification from a survey spectrum is prevented due to the mixing of the Al 2p signal with the Cu 3p peak intensity. However, since these data include the combined intensity for the Al 2s and Cu 3s peaks, an indirect determination for the Al contribution can be made provided two additional pieces of information are also available, namely, the ratio of Al 2p : Al 2s measured from pure Al and similarly the ratio for the Cu 3p : Cu 3s peaks measured from a pure copper sample.

The following analysis shows how the intensity for the Al 2p peak can be calculated given these additional ratios.

Let the intensity for the Cu 3p and Al 2p peaks as measured be

$$I_p = I_{Cu_{3p}} + I_{Al_{2p}}$$

$$I_s = I_{Cu_{3s}} + I_{Al_{2s}}$$

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The ratio calculated from these intensities $R$ is therefore

$$R = \frac{I_{Cu_{3p}} + I_{Al_{2p}}}{I_{Cu_{3s}} + I_{Al_{2s}}}$$

If the spectrum is from pure copper the ratio reduces to

$$R_{Cu} = \frac{I_{Cu_{3p}}}{I_{Cu_{3s}}}$$

Similarly for a spectrum from pure Al the ratio is

$$R_{Al} = \frac{I_{Al_{2p}}}{I_{Al_{2s}}}$$

Provided these two specific ratios are known

$$R = \frac{I_{Cu_{3p}} + I_{Al_{2p}}}{\dfrac{I_{Cu_{3p}}}{R_{Cu}} + \dfrac{I_{Al_{2p}}}{R_{Al}}}$$

$$\Rightarrow R\left(\frac{I_{Cu_{3p}}}{R_{Cu}} + \frac{I_{Al_{2p}}}{R_{Al}}\right) = I_{Cu_{3p}} + I_{Al_{2p}}$$

$$\Rightarrow \frac{R}{R_{Cu}}I_{Cu_{3p}} - I_{Cu_{3p}} = I_{Al_{2p}} - \frac{R}{R_{Al}}I_{Al_{2p}} \Rightarrow \left(\frac{R}{R_{Cu}} - 1\right)I_{Cu_{3p}} = \left(1 - \frac{R}{R_{Al}}\right)I_{Al_{2p}}$$

$$\therefore \frac{I_{Cu_{3p}}}{I_{Al_{2p}}} = \frac{\left(1 - \dfrac{R}{R_{Al}}\right)}{\left(\dfrac{R}{R_{Cu}} - 1\right)}$$

Since

$$I_p = I_{Cu_{3p}} + I_{Al_{2p}} = \frac{\left(1 - \dfrac{R}{R_{Al}}\right)}{\left(\dfrac{R}{R_{Cu}} - 1\right)}I_{Al_{2p}} + I_{Al_{2p}}$$

$$\Rightarrow I_{Al_{2p}} = \frac{I_p}{\left(\dfrac{\left(1 - \dfrac{R}{R_{Al}}\right)}{\left(\dfrac{R}{R_{Cu}} - 1\right)} + 1\right)}$$

Thus provided the ratios $R_{Cu}$ and $R_{Al}$ are determined for an instrument from standard samples, the intensity for the Al signal measured from the p-orbital is calculated using the measured quantities $R$ and $I_p$ determined from the data.

Similarly, the intensity for the copper signal can be determined using

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$$I_{Cu_{3p}} = \frac{I_p}{\left( \dfrac{\left( \dfrac{R}{R_{Cu}} - 1 \right)}{\left( 1 - \dfrac{R}{R_{Al}} \right)} + 1 \right)}$$

Expressions such as these can be included in the Custom Report on the Report Spec property page of the Quantification Parameters dialog window.
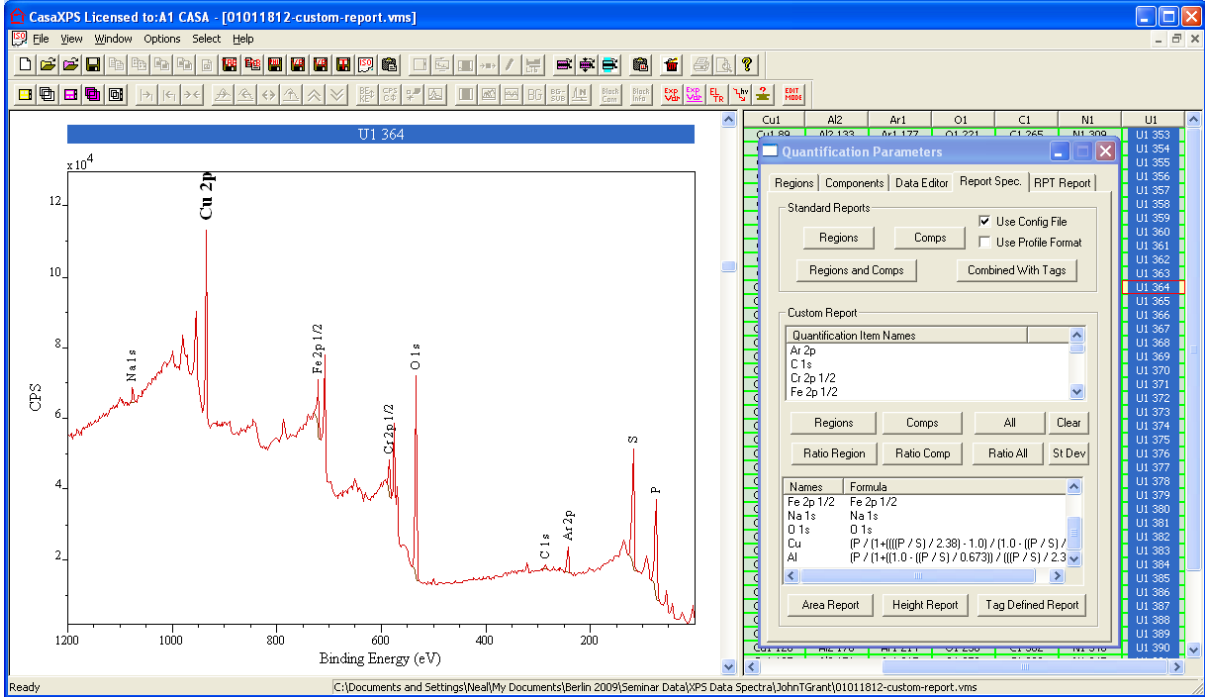


The above example illustrates how a set of regions are used for peaks other than Cu and Al when profiling a material containing both copper and aluminium. The two regions corresponding to the s and p orbitals for Cu and Al are named S and P respectively. The formulae appearing in the custom report are expressed in terms of these two region names. The RSF in each of these regions S and P is set to unity and the RSF for Al 2p and Cu 3p introduced as part of the formulae in the custom report table.

Names and formula for use with the custom report can be prepared and saved in the CasaXPS.CQL directory.



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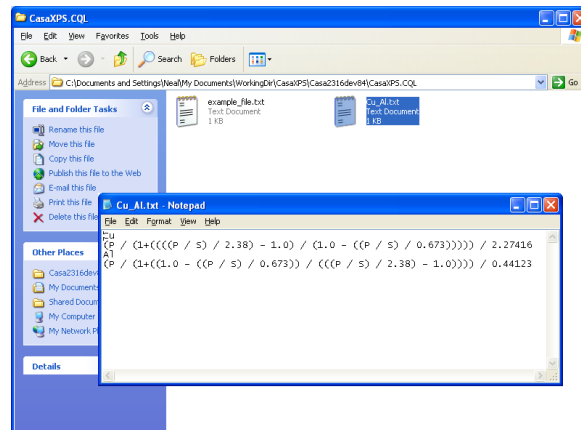
When the heading button labelled Formula is pressed, a dialog window offers a list of the files in the CasaXPS.CQL directory.
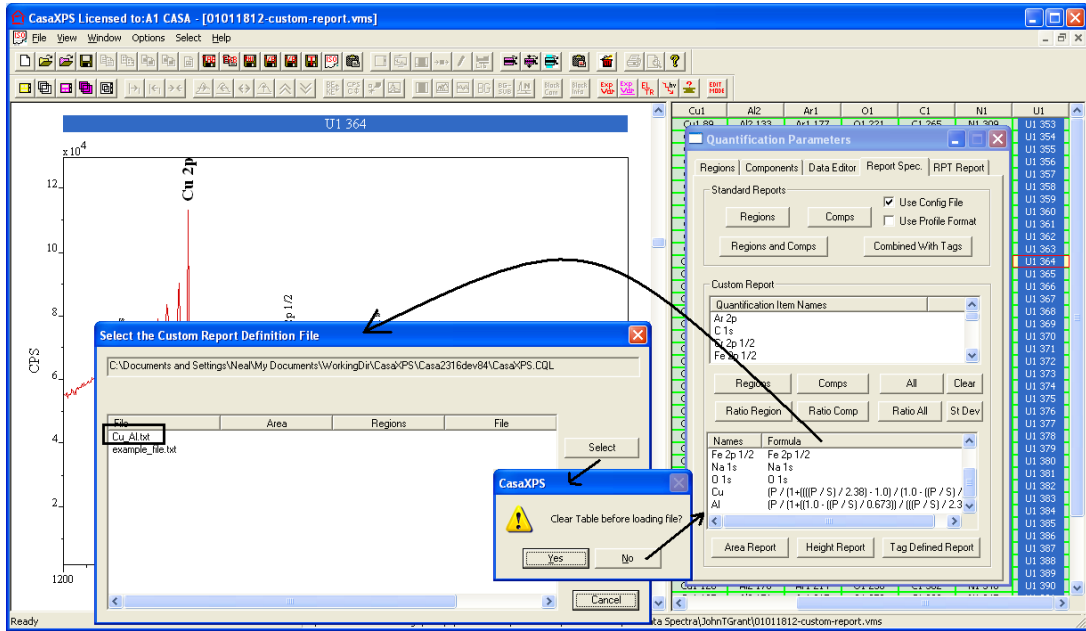


The contents of the selected file are either merged with the existing table or replace the table depending on the response to a dialog window invoked by the Formula button.

The following profile is computed using the intensities from the two regions names S and P to establish the Al and Cu atomic concentration.
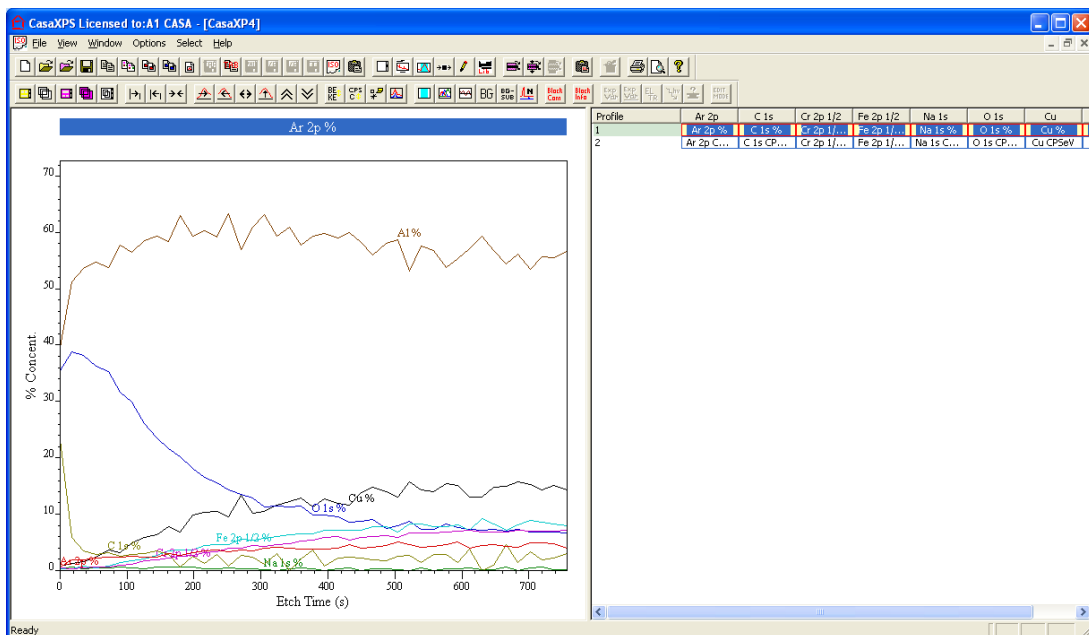


Note: The quality of the profile generated from the Al 2p/Cu 3p peak intensity is determined by the signal to noise for the said peak. If the Cu 2p peak where used instead of the derived Cu 3p, the superior signal to noise for the Cu 2p data for the same acquisition time would be evident in the profile results. To achieve the same quality of trace for Cu based on the Cu 3p data, an acquisition time roughly ten times longer than that used for the Cu 2p peak would be required.

# Standard Report: XPS Spectra containing Copper and Aluminium

The following discussion describes how to calculate scale factors which can be entered into the RSF fields of a region to permits a quantification from a survey spectrum based on the Standard Report option on the Report Spec property page. An advantage of calculating these effective sensitivity factors is a quantification table can be added to spectra displayed in the left-hand pane in the form of annotation.

The spectra used to describe the calculation are measured from a PHI Versa Probe at Vanderbilt University (Bridget Rogers, private communication). Rather than using a copper-aluminium alloy material as the test case, two spectra measured from clean copper and sapphire are summed to provide a simulated Al-Cu spectrum for which the relative proportions are clearly known. Hence the formulae can be validated at the same time as illustrating the approach.
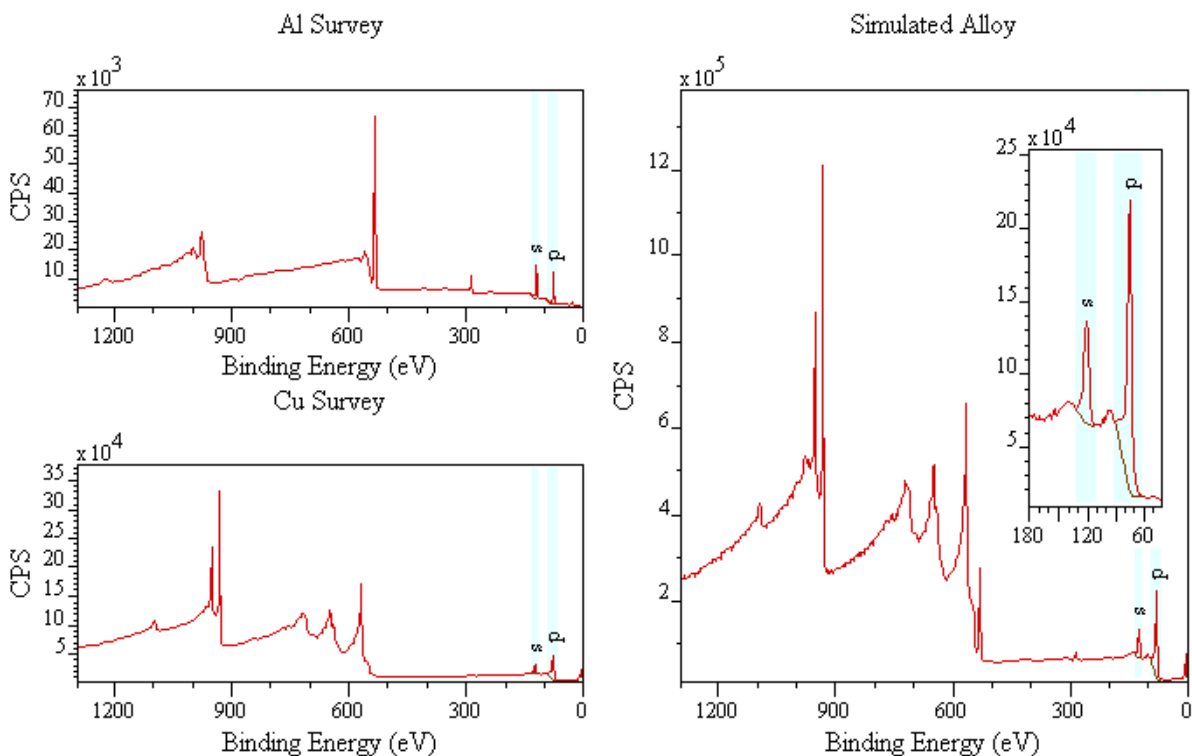


The peak intensity for an Al 2p peak is given by

$$I_{Al_{2p}} = \frac{I_p}{\left( \frac{\left(1 - \frac{R}{R_{Al}}\right)}{\left(\frac{R}{R_{Cu}} - 1\right)} + 1 \right)}$$

where $I_p$ is the intensity measured from the region labelled $p$ on the spectra above. Thus the RSF adjusted aluminium intensity is

$$\frac{I_{Al_{2p}}}{RSF_{Al_{2p}}} = \frac{I_p}{\left(\frac{\left(1 - \frac{R}{R_{Al}}\right)}{\left(\frac{R}{R_{Cu}} - 1\right)} + 1\right) RSF_{Al_{2p}}}$$

Therefore the effective RSF for calculating the amount of Al in the surface from the intensity $I_p$ of the region labelled $p$ is

$$Effective\ Al\ RSF_p = \left(\frac{\left(1 - \frac{R}{R_{Al}}\right)}{\left(\frac{R}{R_{Cu}} - 1\right)} + 1\right) RSF_{Al_{2p}}$$

Similarly for copper

$$Effective\ Cu\ RSF_p = \left(\frac{\left(\frac{R}{R_{Cu}} - 1\right)}{\left(1 - \frac{R}{R_{Al}}\right)} + 1\right) RSF_{Cu_{3p}}$$

To produce a quantification table including the Al and Cu contributions from the $I_p$ peak intensity, the values for $R_{Al}$ and $R_{Cu}$ must be calculated for pure Al and pure Cu survey spectra. The Custom Report can be used to calculate these ratios using regions as shown below defined on the peaks in the Al survey and Cu survey spectra. The values computed from these data are shown in the two text reports.
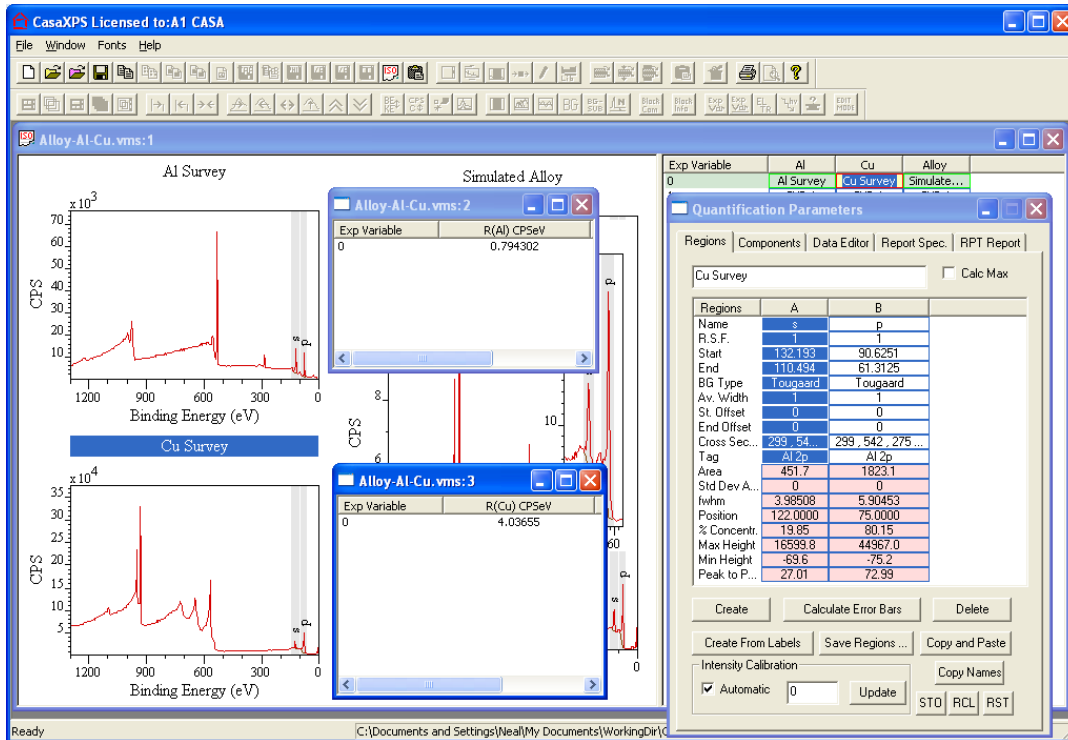


Given the values for $R_{Al}$ and $R_{Cu}$ and the ratio measured from the simulated Cu-Al material, the effective RSFs are computed for the simulated Cu-Al material using the Custom Report. These formulae for the effective RSFs can be saved in a text file in the CasaXPS.CQL directory.
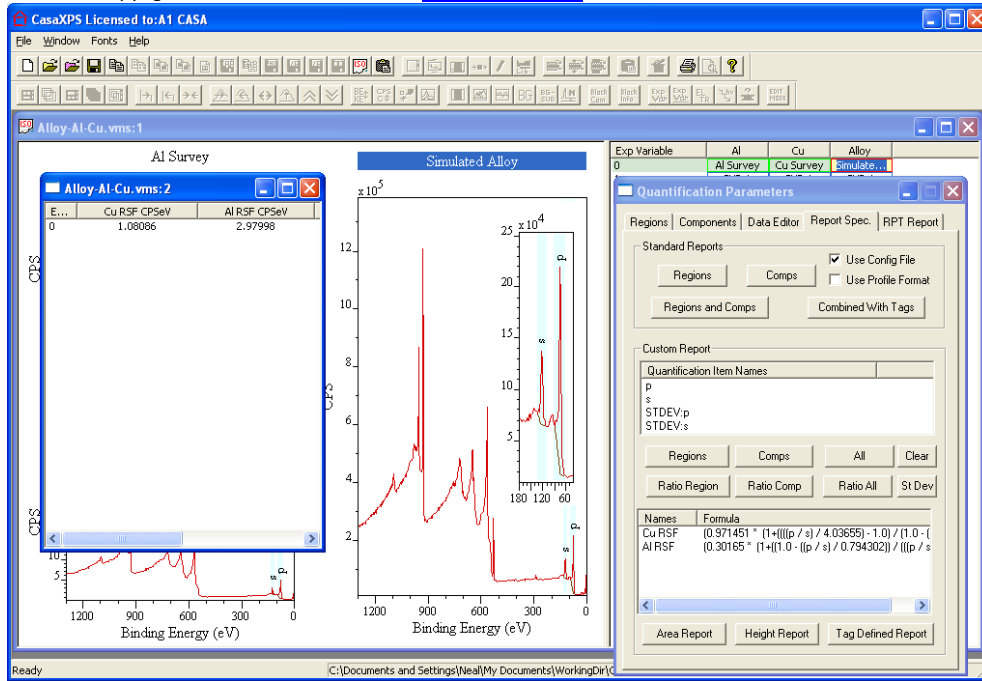
In order to prepare RSF corrected intensities for the Cu and Al signal for use in a quantification table, the peak area for the region labelled $p$ used to calculate the effective RSFs must be used twice within the quantification calculation. To achieve this "sleight of hand", the *skip* background type is used to specify a second quantification region over the same peak. One region in the simulated Al-Cu material is assigned the Al name and Al effective RSF while the second is assigned the Cu name and Cu effective RSF. Apart from the name, the RSF and the *skip* background type, the definition of these two regions is the same.
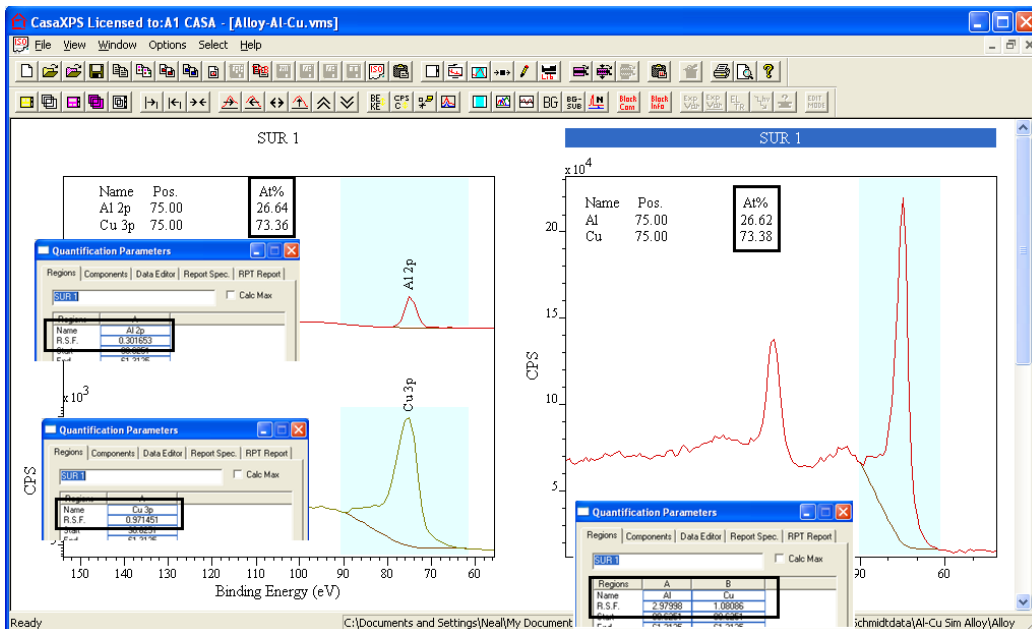


The quantification calculated using the effective RSFs and the summed Al and Cu spectra is the same as when the two individual peaks are quantified and the RSFs are the library RSFs for the PHI Versa Probe instrument.

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