

## Understanding Relative Sensitivity Factors for Doublet Transitions

When quantifying XPS spectra, Relative Sensitivity Factors (RSF) are used to scale the measured peak areas so that variations in the peak areas are representative of the amount of material in the sample surface. An element library typically contains lists of RSFs for XPS transitions. For some transitions more than one peak appears in the data in the form of doublet pairs and, in the case of the default CasaXPS library, three entries are available for each set of doublet peaks: one entry for the combined use of both doublet peaks in a quantification table and two entries for situations where only one of the two possible peaks are used in the quantification. A common cause of erroneous quantification is the inappropriate use of these optional RSF entries.

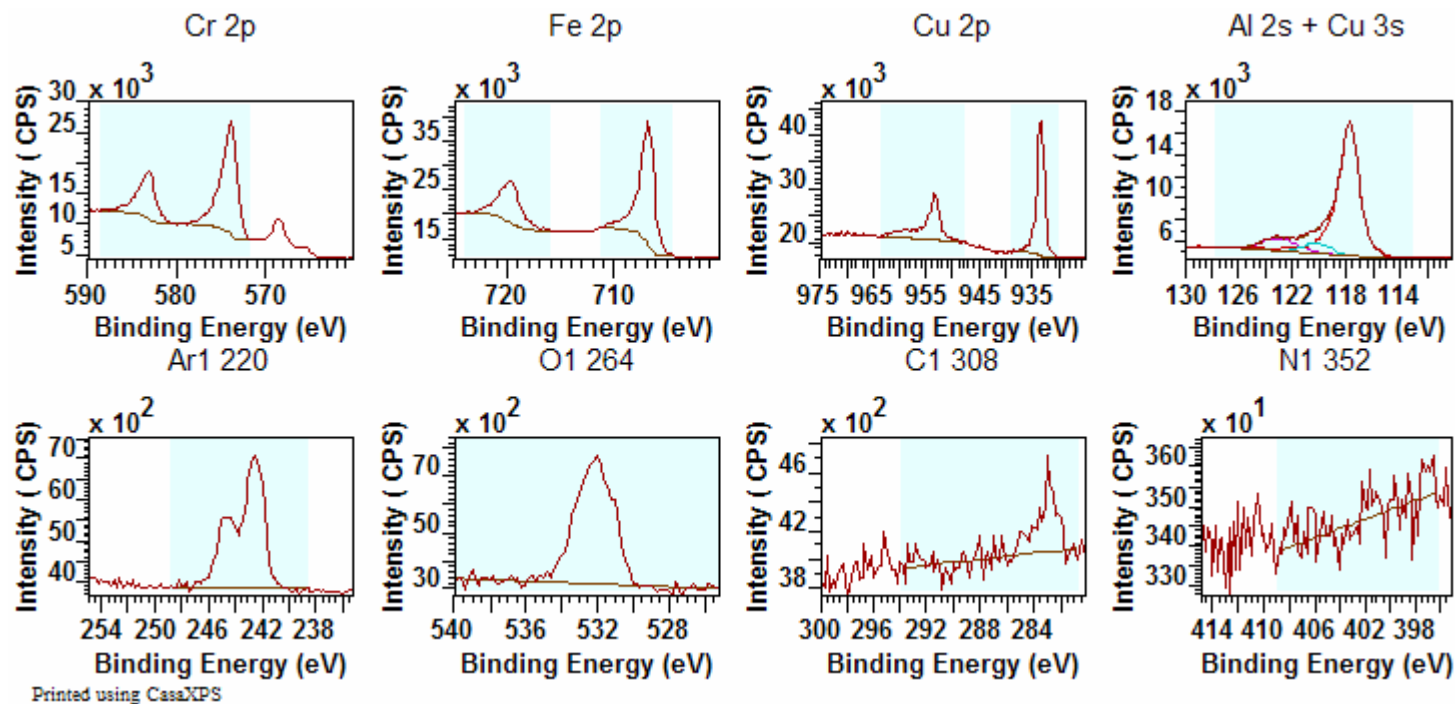


Figure 1: An example of quantification regions and components used to quantify peak areas.

The data in Figure 1 are a set of high resolution spectra where quantification regions and components are used to calculate the area for the peaks. These data illustrate some of the issues associated with XPS quantification as the data includes singlet peaks in the form of O 1s, C 1s, Al 2s and N 1s; as well as doublet pairs: Cr 2p, Cu 2p, Ar 2p and Fe 2p. The spectra are sufficiently complex to involve overlaps such as the Al 2s and Cu 3s, while the Cu 2p<sub>1/2</sub> peak includes signal from a Cr Auger line. When creating a table of percentage atomic concentrations it is important to select the correct RSF for the peak area chosen to measure the given element.

When measuring a transition, from the perspective of signal to noise, it is better to include both peaks from a doublet pair. For the data in Figure 1, the Fe 2p, Cr 2p and Ar 2p transitions are free of interference from other peaks and therefore simple integration regions can be used to measure the peak areas. The Ar 2p doublet peaks overlap each other; however the Cr 2p and Fe 2p peaks do not overlap, thus separate quantification regions are used to measure the area for these resolved doublet peaks. Even though separate regions are used to estimate the peak areas for the two peaks in each of the Cr 2p and the Fe 2p transitions, total RSFs for these transitions are used to scale the raw area calculated from the regions. Similarly, the total RSF is used to scale the Ar 2p doublet peaks, because both peaks from the doublet are used in calculating the peak area for argon. On the other hand, since the Cu 2p<sub>1/2</sub> peak overlaps with the Cr LMM, only the Cu 2p<sub>3/2</sub> peak can be used with ease and so the reduced RSF must be applied to scale the peak area. The quantification table in Table 1 lists the regions and components

used to calculate the atomic concentrations together with the RSFs for each transition.

Note that the peak model used to measure the Al 2s includes a component representing the contribution of the Cu 3s transition to the Al 2s spectrum in Figure 1. Copper is measured using the Cu 2p<sub>3/2</sub> peak therefore the RSF for the Cu 3s component is set to zero so that the component does not appear in Table 1.

Name	R.S.F.	% Conc.
Cr 2p 1/2	10.6041	2.9
Cr 2p 3/2	10.6041	6.2
Fe 2p 1/2	14.8912	2.2
Fe 2p 3/2	14.8912	4.5
Cu 2p 3/2	15.0634	4.4
Al 2s Metal	0.753	61.4
Al 2s Ox	0.753	5.1
Ar 2p	2.65797	5.5
O 1s	2.93	6.2
C1s	1	1.5
N1s	1.8	0.2

**Table 1: Quantification table showing RSFs used to scale the raw peak areas.**

By way of example, an alternative quantification regime might be to use only one of the two possible Fe 2p doublet peaks. The quantification in Table 2 removes the Fe 2p<sub>1/2</sub> region from the calculation by setting the RSF to zero, whilst adjusting the Fe 2p<sub>3/2</sub> RSF to accommodate the absence of the Fe 2p<sub>1/2</sub> peak area from the calculation. Since the ratio of 2p doublet peaks

should be 2:1, the RSF for the Fe 2p<sub>3/2</sub> region is two thirds of the total RSF used in Table 1. In Table 1, the percentage atomic concentration for Fe is split between the two Fe 2p doublet peaks, whereas in Table 2 the entire Fe 2p contribution is estimated using the Fe 2p<sub>3/2</sub> and therefore the same amount of Fe is measured via either approach.

A common misunderstanding is to use both peaks in the calculation, but still assign RSFs for the individual peaks in the doublet. The consequence of using both peaks and the specific RSFs to the individual peaks in the doublet is that the contribution from Fe to the quantification table would be incorrectly increased by a factor of two.

Note: the RSFs used in both Table 1 and Table 2 are Scofield cross-sections adjusted for angular distribution corrections for an instrument with angle of 90° between the analyser and x-ray source.

Name	R.S.F.	% Conc.
Cr 2p 1/2	10.6041	2.9
Cr 2p 3/2	10.6041	6.2
Fe 2p 3/2	9.8064	6.8
Cu 2p 3/2	15.0634	4.4
Al 2s Metal	0.753	61.3
Al 2s Ox	0.753	5.1
Ar 2p	2.65797	5.5
O 1s	2.93	6.2
C1s	1	1.5
N1s	1.8	0.2

Table 2: Fe 2p 3/2 peak is used without the area from the Fe 2p<sub>1/2</sub>.

To further illustrate the issues associated with the uses of the three RSFs associated with doublet peaks, consider the three possible options available when quantifying the Cr 2p doublet shown in Figures 2, 3 and 4. Table 3 shows that the corrected area when measured using any of these three options is approximately the same.

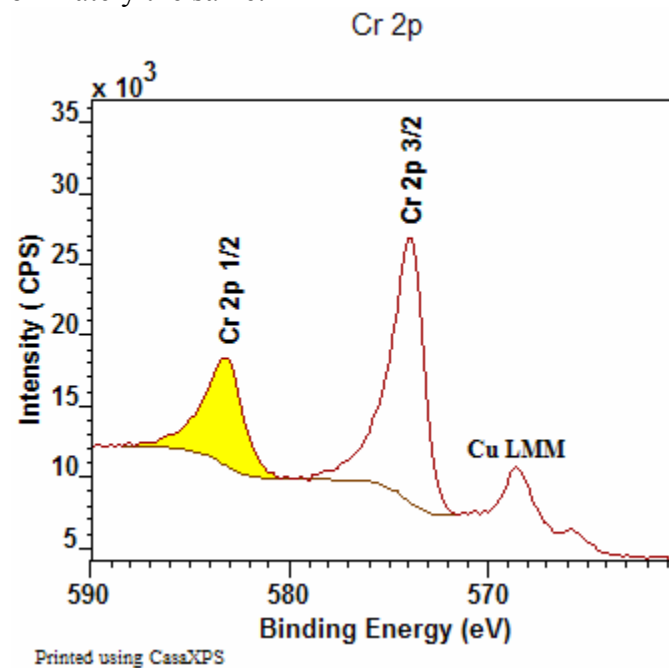
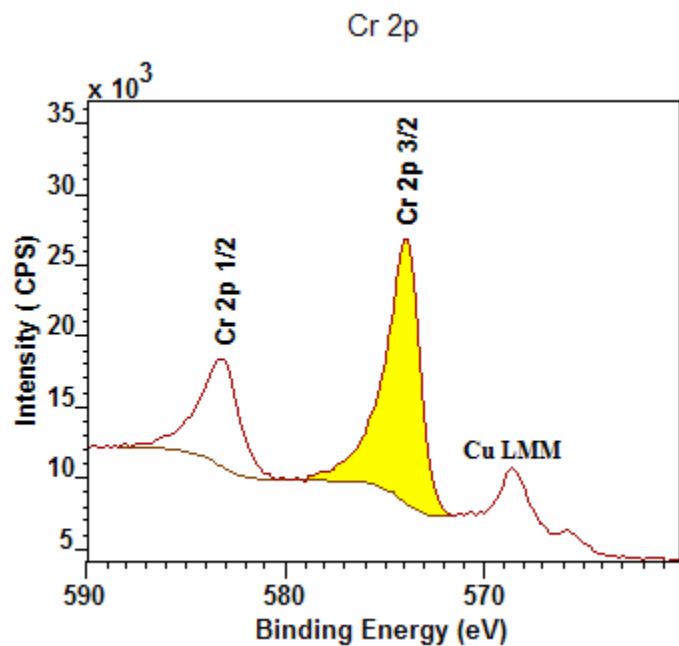


Figure 2: Intensity for Cr calculated from the Cr 2p<sub>1/2</sub> transition.

Cr 2p <sub>1/2</sub> RSF	Raw Area
3.60721	19234.8

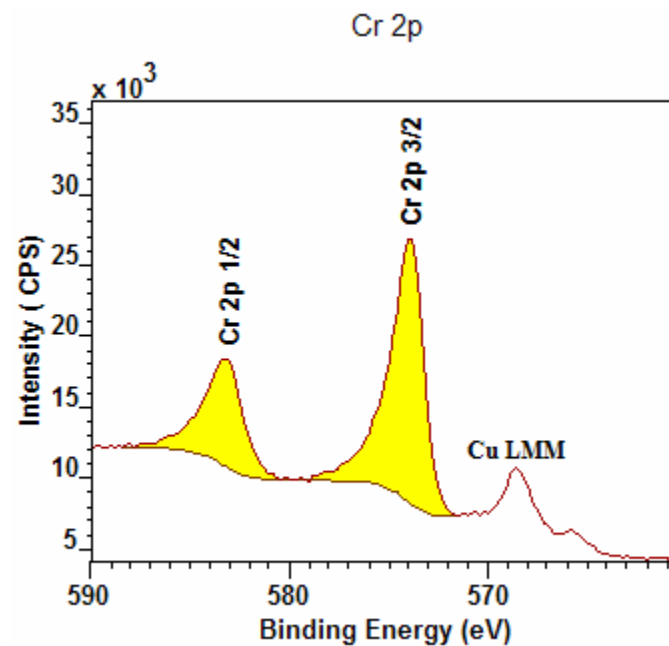


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Figure 3 Intensity for Cr calculated from the Cr 2p<sub>3/2</sub> transition.

Cr 2p<sub>3/2</sub> RSF  
6.9697

Raw Area  
40871.9



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Figure 4 Intensity for Cr calculated from both peaks in the doublet.

Total RSF  
10.6041

Raw Area  
60098.5

Peak	RSF	Raw Area	Corrected Area Raw Area/(RSF*T*MFP)
Cr 2p 1/2	3.60721	19234.8	125.455
Cr 2p 3/2	6.9697	40871.9	138.192
Both Cr 2p Peaks	10.6041	60098.5	133.555

Table 3: Comparison of the intensities calculated from the three different combinations of peak area and RSF for the Cr 2p doublet illustrated in Figure 2 Figure 3 and Figure 4.