Relative Sensitivity Factors for Doublet Pairs

By way of example consider the spectrum in Figure 1. Two peaks from a 2p doublet pair are measured to obtain peak areas p1 and p2. The objective is to scale these areas using relative sensitivity factors such that the intensity relative to the C 1s (Scofield) or F 1s (Wagner/PHI/Kratos) transition is:

$$I_{normalised} = \frac{p1}{S_{2p_{1/2}}} = \frac{p2}{S_{2p_{3/2}}} = \frac{p1 + p2}{S_{2p_{1/2}} + S_{2p_{3/2}}}$$

where the sensitivity factors S are subscripted using the peak assignments. For a 2p doublet pair, the ratio of the $2p_{1/2}$ to $2p_{3/2}$ peak areas should be in the ratio 1:2, which is determined from the multiplicity of the degenerate $2p_{1/2}$ to $2p_{3/2}$ electron configurations of the final state following emission of a 2p electron. Therefore, if both peaks are used to measure the intensity of a transition, the sum of the two sensitivity factors should be used to divide the total intensity from both peaks.

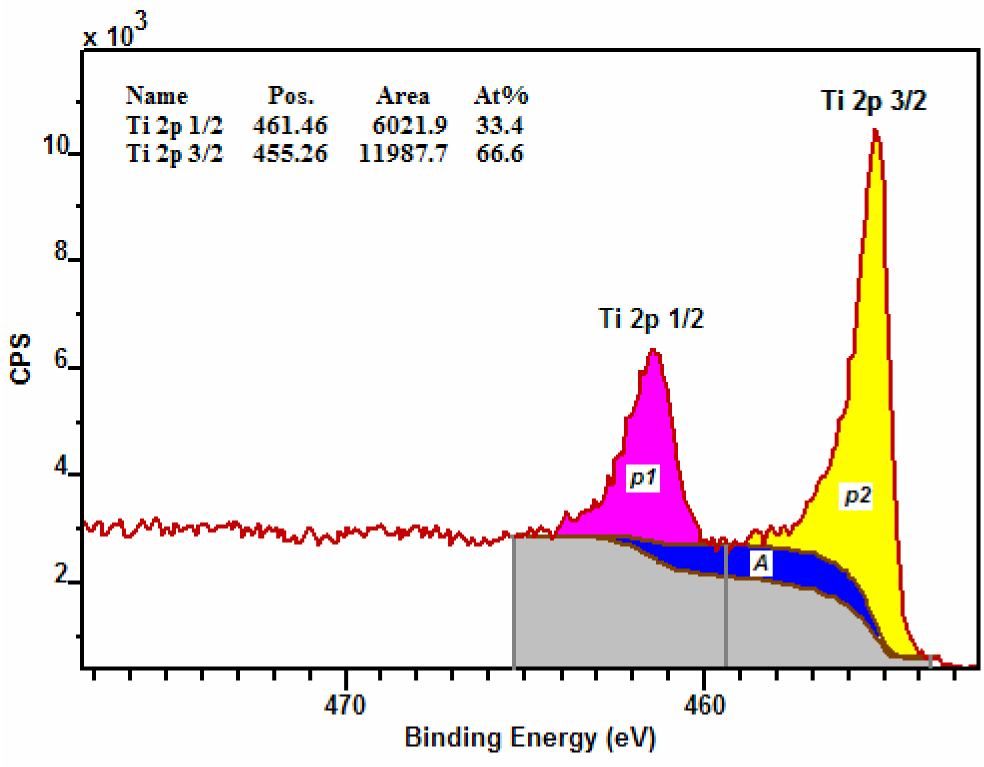

Figure 1: Ti 2p doublet pair. The RSF used in the quantification table is set to unity in order to illustrate the predicted 1:2 ratio of these peaks. The areas p1 and p2 are calculated using two regions each with Shirley backgrounds. The area labeled A is the difference between using a single region with a Shirley background and two separate regions. Data supplied by Elise Pegg, Bioengineering Group, University of Nottingham.

The main source for confusion with library sensitivity factors occurs where, for historical reasons, the library only contains a single RSF for an element and it is not clear whether the value is for use with the sum of the peak areas from a doublet pair or whether the RSF is appropriate for only one peak from the doublet. If a library contains two RSF values for a given transition, a simple test is to ratio the pair of RSF values. If the values are for scaling the individual peaks in a doublet, then for p-doublets the ratio should be 1:2, for d-doublets the ratio should be 2:3 and for f-doublets the ratio should be 3:4. If the library only contains a single value for a doublet pair, a comparison with the values in the Scofield library is a good indicator of how the RSF should be used. For example, the Al anode x-ray Scofield cross-sections for the Ti 2p doublet are 2.59:5.22 (≈ 1:2) and so the Scofield RSF for the combined T 2p peaks is 7.81. The Kratos library contains an RSF of 2.001 for the Ti 2p transition. The Scofield values are relative to the C 1s transition, whereas the Kratos/PHI/Wagner RSFs are relative to the F 1s transition, so dividing the Kratos value by the Kratos RSF for C 1s, namely 0.278, results in a value of 7.2 for the Kratos Ti 2p RSF relative to C 1s. For this example, the value in the Kratos library labeled Ti 2p is most probably appropriate for the combined doublet, sine 2.001/0.278=7.2 is closer to the Scofield cross-section for the combined peaks (7.81) than the cross-section for either of the individual peaks (2.59 or 5.22). The Kratos RSFs include instrumental influences, therefore this comparison may not always apply, but for the most part will be a reasonable indicator.

Given the RSF for the combined areas from a doublet pair the RSF for individual peaks can be estimated as follows:

Core-level *l*	Minor Peak	Major Peak
p	RSF/3	RSF*2/3
d	RSF*2/5	RSF*3/5
f	RSF*3/7	RSF*4/7