

Quantitative Chemical State XPS Analysis of First Row Transition Metals, Oxides and Hydroxides

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Abstract. Practical quantitative chemical state X-ray photoelectron spectroscopy (XPS) analysis of first row transition metals, oxides and hydroxides is challenging due to the complexity of their M 2p spectra. Complex multiplet splitting, shake-up and plasmon loss structure can play a role in the interpretation of the chemical states present. This paper will show practical curve fitting procedures for the quantitative measurement of different chemical states for metal oxides and hydroxides from a survey of transition metals. It will also discuss some of the limitations and pitfalls present as well as give practical examples of their successful use. These curve-fitting procedures are based on 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) fitting of multiplet split spectra based on spectra of numerous reference materials and theoretical modelling, 4) spectral subtractions routines, again using reference spectra, and 5) specific literature references where fitting procedures are available.

1. Introduction

Chemical state determination using X-ray photoelectron spectroscopy (XPS) has become routine for most of the elements in the periodic table. Binding energy databases, such as the NIST Database [1] or the Phi Handbook [2], generally provide sufficient data for the determination of chemical state for uncomplicated (i.e. single peak) spectra. However, the M 2p spectra from the transition metals pose a number of problems that these databases do not adequately cover, specifically, shake-up structure, multiplet splitting and plasmon loss structure, all of which can complicate interpretation of the chemical states present.

There is a finite probability that an ion (after photoionization) will be left in an excited state a few eV above the ground state. When this happens, the KE of the emitted photoelectron is reduced and

will be seen as a “shake-up” peak at a higher binding energy than the main line. Shake up lines are common with paramagnetic states. Multiplet splitting arises when an atom has unpaired electrons (eg. Cr(III) – $3p^63d^3$). When a core electron vacancy is made by photoionization, there can be coupling between the unpaired electron in the core with the unpaired electrons in the outer shell. This can create a number of final states which will be seen in the photoelectron spectrum. For some materials, where plasmon loss peaks occur, there is an enhanced probability for loss of a specific amount of energy due to the interaction between the photoelectron and other electrons. For conductive metals, the energy loss (plasmon) to the conduction electrons occurs in well-defined quanta arising from group oscillations of the conduction electrons. Plasmons attributed to the bulk of the material and its surface can sometimes be separately identified. For example, Ni 2p spectra must include plasmon loss structure (both bulk and surface) for the metal in their deconvolution.

This paper outlines some recent spectral curve fitting procedures developed for elucidating quantitative chemical state information from a variety of transition metal-containing materials. The fitting procedures measure the sum of the photoelectrons for each chemical state. This can then be directly related to the percentage amount of each chemical state at the surface of a sample. The data used for each element are based on one or a combination of 1) analysis of quality standard samples taken over the course of number of years on a state-of-the-art Kratos Axis Ultra XPS spectrometer, 2) a survey of literature databases and/or a compilation of literature references, 3) fitting of multiplet split spectra based on spectra of numerous reference materials and based on the theoretical modelling of Gupta and Sen [3,4], 4) spectral subtractions routines again using reference spectra, and 5) specific literature references where fitting procedures are available (although these are very rare).

2. Experimental

The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al $K\alpha$ source (15mA, 14kV). The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au $4f_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu $2p_{3/2}$ line of metallic copper. The Kratos charge neutralizer system was used on all specimens. High-resolution spectra were obtained using either a 10, 20 eV or 40 eV pass energy and an analysis area of $\sim 300 \times 700 \mu\text{m}$. Spectra were analysed using CasaXPS software [5] (version 2.2.107).

3. Results and Discussion

3.1. Chromium

Fitting parameters for chromium $2p_{3/2}$ spectra are based on spectra taken from a series of well-characterized standard compounds [6]. Fitting parameters that can determine Cr(0), Cr(III) oxide, Cr(III) hydroxide and Cr(VI) components were determined and take into account asymmetry in the metal peak, a broader envelope of peaks attributed to multiplet splitting of the Cr(III) compounds and a single peak (no unpaired electrons) for Cr(VI) compounds. Cr(III) species can be further divided into the oxide, which will show discrete multiplet structure, and the hydroxide which shows only a broad peak-shape. The asymmetry in the metal peak is defined here by a Gaussian/Lorentzian product formula modified by an asymmetric form (supplied by CasaXPS software[5]) and is based on spectra from an argon ion sputter cleaned pure metal surface. The FWHM

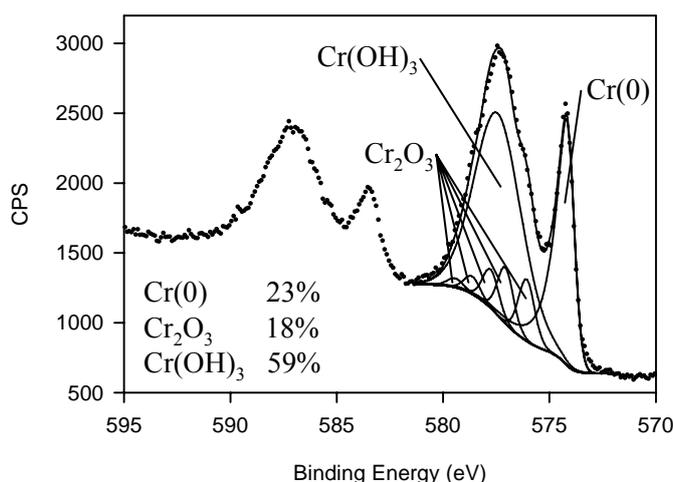


Figure 1. Cr 2p spectrum of a treated decorative chrome plating using the final fitting parameters from reference 6. Percentage of each component shown.

for the metal will depend on the instrument used and should be measured for a particular instrument type. Analysis of the metal peak will also give a good estimate of multiplet splitting peak-widths as the FWHM of the metal peak generally matches that of the individual multiplet peaks under similar spectrometer conditions. Peak-widths for the Kratos Axis Ultra set at a pass energy of 20 eV are around 0.88 eV for the metal and five individual Cr(III) oxide multiplet peaks, while the hydroxide peak is around 2.6 eV. Quantification of Cr(VI) species is limited by the overlap with the multiplet splitting of the Cr(III) species. This likely raises the detection limits for Cr(VI) in a mostly Cr(III) matrix to around 10% of total chromium. Any contribution attributed to Cr(VI) below that should be treated as “not detected”. An example of this fitting is presented in Figure 1.

3.2. Copper

This method [7] of Cu(I):Cu(II) determination depends on shake-up peaks that are present in the spectra of d^9 Cu(II) containing samples but are absent in d^{10} Cu(I) spectra. Shake-up peaks may occur when the outgoing photoelectron simultaneously interacts with a valence electron and excites it (shakes it up) to a higher-energy level. The kinetic energy of the core electron is then slightly reduced giving a satellite structure a few eV below (above on the binding energy scale) the core level position [8]. Hence, the main emission line (A) (see Figure 2) contains both Cu(II) (A1) and Cu(I) (A2) contributions but the satellite intensity (B) is entirely from Cu(II). The total intensity from Cu(II) species is represented in the combination of the signals from the direct photoemission (A1) and the shaken-up photoemission (B).

Accurate surface Cu(I):Cu(II) ratios for samples containing a mixture of (surface) Cu(I) and Cu(II) relies on determining an accurate ratio of the main peak /shake-up peak areas (A_1/B_s) for a 100% pure Cu(II) sample(S). With a reliable value of A_1/B_s obtained for $Cu(OH)_2$ (where all copper present is in the Cu(II) state), the relative concentrations of Cu(I) and Cu(II) species present on a surface that contains both species can be obtained by the following simple equations:

$$\% \text{ Cu(I)} = A_2/(A+B)*100 = (A-A_1)/(A+B)*100 = (A-(A_1/B_s)B)/(A+B)*100 \quad (1)$$

$$\% \text{ Cu(II)} = (B+A_1)/(A+B)*100 = B(1+(A_1/B_s))/(A+B)*100 \quad (2)$$

where B is the area of the shake-up peak and A is the total area of the main peak.

In order to determine accurate values of A_1/B_s , seven Cu 2p_{3/2} analyses of pure $Cu(OH)_2$ (Alfa Aesar) were obtained. Analyses were carried out on the various $Cu(OH)_2$ samples at acquisition times of generally less than a few minutes as it has been shown that reduction of $Cu(OH)_2$ can occur after extended X-ray exposure [9]. Studies in this lab suggest that after X-ray exposures of 3 hours up to 10% of $Cu(OH)_2$ has been reduced to Cu(I). At pass energies of 20 eV and 40 eV, A_1/B_s values of

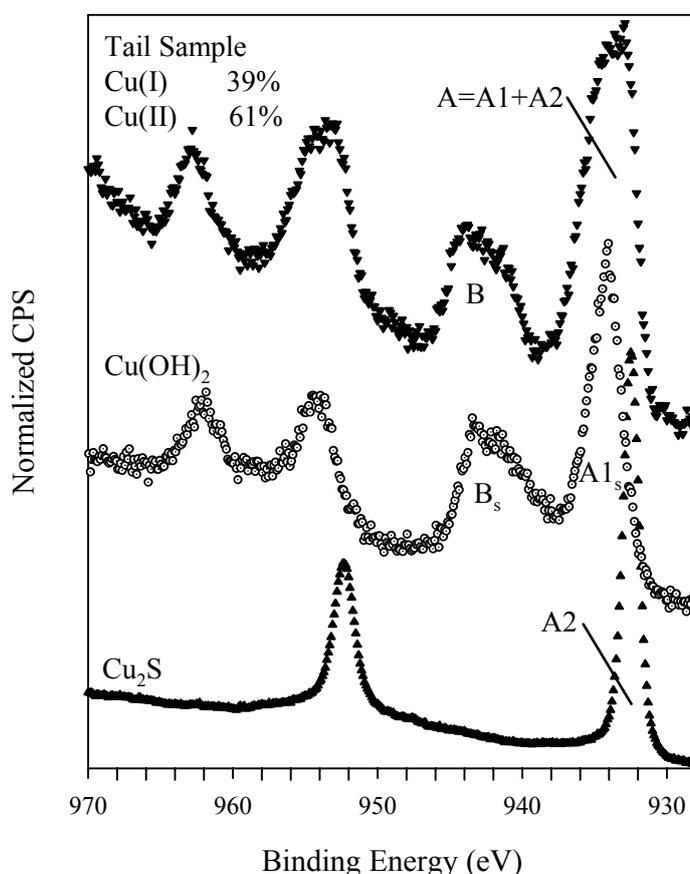


Figure 2. Cu 2p spectra for an unoxidized Cu_2S surface, $Cu(OH)_2$ standard used for A_1/B_s determination and a spectrum from a flotation process tailing sample with the amount of oxidation of the Cu_2S surface calculated.

1.57±0.1 and 1.59±0.1 were found, respectively. Figure 2 shows spectra for an unoxidized Cu₂S surface, Cu(OH)₂ standard used for A_{1s}/B_s determination and a spectrum from a mine tailing sample with the amount of oxidation of the Cu₂S surface calculated.

3.3. Titanium

Initial fitting parameters for the titanium 2p peak were developed using averaged binding energy (BE) data and 2p_{1/2} – 2p_{3/2} splitting data from the NIST XPS Database.¹ As well, data from readily available standard samples (metal, TiO₂) were used to clarify the peak-widths, splitting ($\Delta=6.08$ eV for Ti(0), $\Delta=5.72$ eV for Ti(IV)) and shapes (asymmetric for the metallic component). An example of the use of these parameters is presented for a mixed oxidation state titanium-containing sample in Figure 3. Although C1s set to 284.8 eV can be used as an internal charge correction it is also possible in this case to use the Ti 2p_{3/2} metal peak set at 453.9 eV or the clearly defined Ti(IV) (TiO₂) 2p_{3/2} peak set at 458.6 eV.

The Ti 2p_{1/2} peak for each species is constrained to be at a fixed energy above the Ti 2p_{3/2} peak. The intensity ratio of the Ti 2p_{3/2} and Ti 2p_{1/2} peaks are constrained to 2:1 which is consistent with the expected ratio of $(2j_1+1)/(2j_2+1)$, where j_1 and j_2 represent the coupled orbital (l) and spin (s) angular momentum quantum numbers from respective spin-up and spin-down states of the unpaired core electron which remains after photoionization [10]. The FWHM's for the metal and Ti(IV) peaks are derived from the standard sample analyses. The FWHM's for Ti(II) (at a BE of 455.4 eV) and Ti(III) (at a BE of 457.2 eV), which are likely structurally loosely ordered, are constrained to have equal width to each other and are generally slightly broader than the well ordered Ti(IV) oxide peaks.

4. Conclusions

This paper shows a few examples where detailed fitting procedures can be used to quantify various chemical states in transition metals. Due to limited space for these proceedings a full description of procedures for these and other transition metal 2p spectra will follow in a subsequent full paper.

5. References

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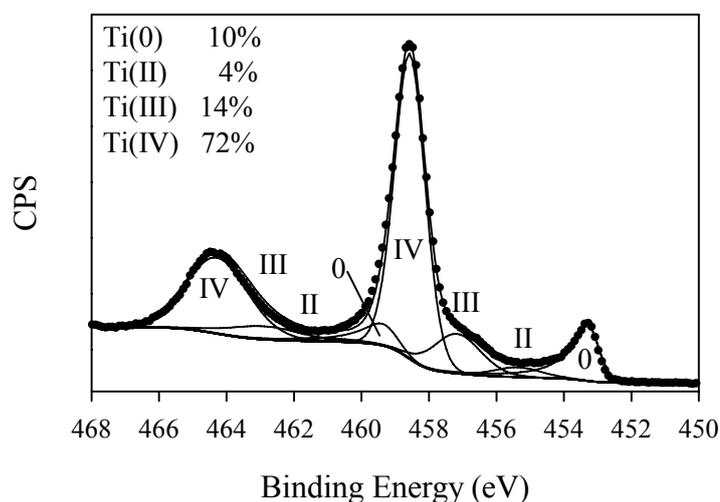


Figure 3. Ti 2p spectrum of an electro-polished titanium metal surface with chemical states quantified. Peak widths, area ratios, Ti 2p_{3/2}–2p_{1/2} splits, peak-shapes and positions are defined by a mix of literature values, theory, and analysis of standard samples.