Improved Accuracy of Quantitative XPS Analysis by Using Estimated Spectrometer-Transmission Functions with UNIFIT 2004

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1. Introduction

Results of quantification from XPS data of varied specimen settings differ up to 30% using Wagner sensivity factors (see Fig. 1). Both, the estimation of the transmission function T of the different specimen settings and the introduction of the product of s, ? and T as sensitivity factor q – transmission cross section of Scofield, ? – incident mean free path – may reduce the uncertainties of less than 10%.

In this paper we present the theoretical background of two methods for the estimation of the transmission function. As example, illustration the practicability of the presented methods. Finally, we give recommendations that might be helpful to minimize errors of quantification.

2. Theoretical basis

The concentrations c_i of an element is defined as:

\[ c_i = \frac{n_i}{\sum n_j} \]

with the intensity n_i, the excitation cross section s_i the mean free path ? and the transmission function T. If we accept that s_i and ? are well-known data, the problem is reduced to determine the transmission function T.

2.1. Method 1: survey spectra approach SSA

For the survey spectra approach, the reference spectra S_i (Au, Ag, Cu) measured on the Monochromator Spectrometer E 150 of SAE, were added to the measured spectra M_i:

\[ T(E) = \frac{S_i(E)}{M_i(E)} \]

The model function T is given by:

\[ T(E) = \frac{s_i(E) + a_i(E) + b_i(E)}{s_i(E) + a_i(E) + b_i(E)} \]

with the parameters a_i, b_i. The demanded function T can be estimated by minimizing of \( T(E) \) using the Marquardt-Levenberg algorithm:

\[ K = \sum (\frac{S_i(E)}{M_i(E)}) - T(E) \]

2.2. Method 2: quantified peak areas approach QPA

Not for all spectrometer settings reference areas are available. In particular, strong matrix variations (Th < 20%) change the form of the transmission function strongly. The transmission function can be calculated in terms of the ratio of normalized intensities from the Si4, Al2O3, Al, Ag, Ag2O, Cu, Cu2O, Cr2O3, Fe, Fe2O3, Ge, GeO2, Ni90Cr10 standard peaks Au, Ag, Cu and Ge.

While the assumption that a linear combination of two base functions of the transmission function T can be determined by minimizing of EK (Eq. 5):

\[ EK = \sum \left( \frac{S_i(E)}{M_i(E)} - T(E) \right)^2 \]

The normalized intensities \( n_i \) are defined as:

\[ n_i = \frac{I_i(E)}{\sum J_i} \]

The method QPA can be used for all types of XPS spectrometers and specimen settings.

3. Estimation of transmission functions of the spectrometer ESCALAB 200 iXL

All investigations were made on the spectrometer ESCALAB 200 iXL. This spectrometer is equipped with a 100“ hemispherical analyser, 6 channel electron multipliers and a set of 2 mechanical spectrometers. For the first method, we used a set of 81 survey spectra. For this study we used an AlMg-Twin model (AlMg Twin) and a component spectrometer Al-Maxus. In practice, counting rates up to 6 MHz may be used with a electronics better than 10%. The energy scale was calibrated to ± 50 eV. The instrument was operated in the constant T-mode of 100 eV and 50 eV. All spectra were acquired in the mode “Multi Sample Acquisition” with the same number of accumulations per region.

The reference samples Au, Ag and Cu in this study were pristine, i.e., Ge was a crystalline source. All samples were sputtered with 5 keV Ar ions to remove contamination and to destroy the crystalline structure of the samples.

Three combinations of the source (AlMg Twin, Al-Maxus, pass energy 100 eV) were used and the transmission function \( T(E) \) was used to test the ratio Ni 2p/Ni 3p to 1. The estimated transmission functions \( T(E) \) were compared to reference samples such asNi90Cr10, SAE 150LAX, E = 10 eV, and SAE 150LAX, E = 50 eV, which were studied (see Fig. 3a – 3c).

The alloy Ni90Cr10 is used as the positive pole of the K line generator (Kalpha generator) and the negative pole is made of the Ni90Cr10 alloy. A hemispherical analyser, 6 channel electron multiplier, the pass energy of 100 eV, the range of 2000 eV per scan, and an optimized signal-to-noise ratio were selected for the Ni90Cr10 alloy.

Transmission function / a.u.

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>T(E)</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>40</td>
<td>0.6</td>
</tr>
<tr>
<td>60</td>
<td>0.7</td>
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4. Test of T(E) on Ni90Cr10

The alloy Ni90Cr10 is used as the positive pole of the K line generator. A typical XPS spectrum of Ni90Cr10 shows Ni 2p at 850 eV, Ni 3p at 640 eV, Ni 3p at 600 eV, Ni 3p at 585 eV and Ni 3p at 570 eV. A normalized relative quantification of Ni90Cr10 should result in the ratio 0.894/0.106. Additionally, the sample was used to test the ratio Ni 2p/Ni 3p to 1.

Result:

The estimated transmission function T(E) of the spectrometer ESCALAB 200 iXL of different settings.

5. Using UNIFIT 2004

The subroutine “Calibration Linearity Scale” enables to determine the transmission function of any XPS spectrometer in two different ways. The resulting functions can be stored, printed, and applied to the concentration analysis routine.

6. Summary

Considerable improvement of the quantification from XPS data using the SSA and QPA for the estimation of the transmission function \( T(E) \) was obtained for different spectrometer settings. In order to reduce the uncertainty of the quantification the following recommendations should be considered:

1. estimation of the transmission function for different spectrometer settings
2. using of values of Scofield or Brian
3. use of the recommended values from the NIST database
4. quantification from relative peak intensities derived from instead background calculation or peak fits with adjustable background
5. use the product of c, T and ? as sensitivity factor

The software integrated in the software UNIFIT 2004 allows for calibration of the transmission function of any XPS spectrometer. The obtained data may be used for the quantification.