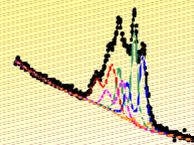


# Improved Accuracy of Quantitative XPS Analysis by Using Estimated Spectrometer-Transmission Functions with UNIFIT 2004

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## 1. Introduction

Results of quantification from XPS data of varied spectrometer settings differ up to 50% using Wagner sensitivity factors (see Fig. 1). Both, the estimation of the transmission function  $T$  of the different spectrometer settings and the introduction of the product of  $s_i$ ,  $\tau$  and  $T$  as sensitivity factor  $\epsilon_i = \text{ionisation cross section of Scofield} \cdot \tau \cdot \text{inelastic mean free path}$  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. An example illuminates the practicability of the presented methods. Finally we give recommendations that might be helpful to minimise errors of quantification.

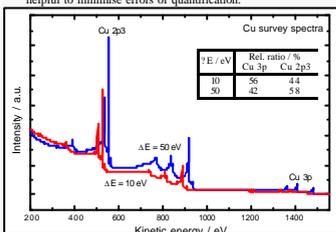


Fig. 1. Comparison of Cu survey spectra measured with Al Twin, Large Area XL,  $\tau E = 10 \text{ eV}$  (red line) and  $\tau E = 50 \text{ eV}$  (blue line). The spectra are normalized of 1/1000 eV. The red spectrum is shifted of 30 eV. The table shows the quantification using Wagner sensitivity factors.

## 2. Theoretical basis

The concentration  $c_i$  of an element  $i$  is defined as

$$c_i = \frac{I_i / (s_i \cdot T_i)}{\sum_j I_j / (s_j \cdot T_j)} \quad (1)$$

with the intensity  $I$ , the ionisation cross section  $s$ , the mean free path  $\lambda$  and the transmission function  $T$ . If we accept that  $s$  and  $\lambda$  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 SSA the reference spectra  $S(E)$  from Au, Ag, and Cu measured on the Metrology Spectrometer II of NPL were adapted to the measured spectra  $M$  writing

$$M(E) = T(E) \cdot S(E) \quad (2)$$

The model function of  $T$  is given by

$$T(E) = a_0 + a_1 e^{-a_2 E} + a_3 e^{-a_4 E} + a_5 e^{-a_6 E} + b_1 E^{b_2} \quad (3)$$

with the fit parameters  $a_0, \dots, b_2$ . The demanded function  $T$  can be estimated by minimizing of  $\chi^2$  using the Marquardt algorithm.

$$\chi^2 = \sum \frac{[S(E) \cdot T(E, a_0, a_1, a_2, a_3, a_4, a_5, b_1, b_2) - M(E)]^2}{M(E)} \quad (4)$$

### 2.2. Method 2: quantified peak-area approach QPA

Not for all spectrometer settings reference functions are available. In particular, strong internal scattering ( $\tau E < 20 \text{ eV}$ ) changes the form of the transmission function strongly. The transmission function can be estimated in such case by means of normalized intensities from Au 4f, Au 4d, Au 4p<sub>3/2</sub>, Ag 3d, Ag 3p<sub>3/2</sub>, Cu 3p, Cu 2p<sub>3/2</sub>, Ge 3p and Ge 2p<sub>3/2</sub> lines measured for Mg Ka and Al Ka X-rays. With the assumption that a relative quantification of two lines of a pure element gives 1,  $T$  can be determined by minimizing of ES of Eq. (5).

$$ES = \frac{\begin{pmatrix} T(0.151) \cdot \epsilon_{Au}(0.403) \\ T(0.403) \cdot \epsilon_{Au}(1.158) \end{pmatrix} \cdot \begin{pmatrix} T(0.940) \cdot \epsilon_{Ag}(0.403) \\ T(0.940) \cdot \epsilon_{Ag}(0.940) \end{pmatrix} \cdot \begin{pmatrix} T(1.151) \cdot \epsilon_{Cu}(0.940) \\ T(1.151) \cdot \epsilon_{Cu}(1.158) \end{pmatrix}}{\begin{pmatrix} T(0.118) \cdot \epsilon_{Cu}(0.940) \\ T(0.118) \cdot \epsilon_{Cu}(1.158) \end{pmatrix} \cdot \begin{pmatrix} T(0.889) \cdot \epsilon_{Cu}(0.940) \\ T(0.889) \cdot \epsilon_{Cu}(1.158) \end{pmatrix} \cdot \begin{pmatrix} T(0.889) \cdot \epsilon_{Cu}(0.940) \\ T(0.889) \cdot \epsilon_{Cu}(1.158) \end{pmatrix}} + \frac{\begin{pmatrix} T(0.411) \cdot \epsilon_{Cu}(0.554) \\ T(0.554) \cdot \epsilon_{Cu}(1.411) \end{pmatrix} \cdot \begin{pmatrix} T(0.178) \cdot \epsilon_{Cu}(0.321) \\ T(0.321) \cdot \epsilon_{Cu}(0.178) \end{pmatrix} \cdot \begin{pmatrix} T(0.458) \cdot \epsilon_{Cu}(0.270) \\ T(0.270) \cdot \epsilon_{Cu}(0.458) \end{pmatrix}}{\begin{pmatrix} T(0.118) \cdot \epsilon_{Cu}(0.940) \\ T(0.118) \cdot \epsilon_{Cu}(1.158) \end{pmatrix} \cdot \begin{pmatrix} T(0.889) \cdot \epsilon_{Cu}(0.940) \\ T(0.889) \cdot \epsilon_{Cu}(1.158) \end{pmatrix} \cdot \begin{pmatrix} T(0.889) \cdot \epsilon_{Cu}(0.940) \\ T(0.889) \cdot \epsilon_{Cu}(1.158) \end{pmatrix}} \quad (5)$$

The normalized intensities  $r$  are defined as

$$r_i = \frac{I_i / (s_i \cdot I)}{\sum_j I_j / (s_j \cdot I)} \quad (6)$$

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

## 3. Estimation of transmission functions of the spectrometer ESCALAB 220 iXL

All investigations were made on the spectrometer ESCALAB 220 iXL. This spectrometer is equipped with a 180° hemispherical analyser, 6 channel electron multipliers and a set of 2 mechanical apertures, 1 magnetic and 6 electrical lenses. The X-ray sources used for this study were an Al/Mg twin anode (Al/Mg Twin) and a monochromatic Al source (Al Mono). In practice, counting rates up to 6 Mc/s may be used with a linearity better than 1%. The energy scale was calibrated to  $\pm 0.1 \text{ eV}$ . The instrument was operated in the constant  $\tau E$  mode of 10 eV and 50 eV. All spectra were recorded 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 metallic foils. Ge was a crystalline wafer. All samples were sputtered with 5 keV argon ions to remove contaminations and to destroy the crystalline structure of Ge. Eight combinations of X-ray source (Al/Mg Twin, Al Mono), pass energy ( $\tau E = 10 \text{ eV}$ ,  $\tau E = 50 \text{ eV}$ ) and lens (Large Area LAE, Large Area XL LAX, Small Area 150 SAE 150) were studied (see Fig. 3a - 3c). The transmission functions  $T(E)$  were tested on the reference samples. Fig. 2 shows the examples for Al/Mg Twin and  $\tau E = 10 \text{ eV}$ .

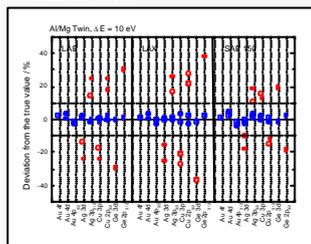


Fig. 2. Comparison of deviations of quantification of the reference samples using own estimated  $T(E)$  (blue symbols) and Wagner sensitivity factors (red symbols) from the true value. Squares: excited by Al Ka; Circles: excited by Mg Ka.

## 4. Test of $T(E)$ on Ni90Cr10

The alloy Ni90Cr10 is used as the positive pol of the K type thermocouple. A typical analysis gives 88.3 at.% Ni, 10.5 at.% Cr, 0.16 at.% Fe, 1.04 at.% Si and traces of Co. A normalized relative quantification of Ni/Cr should result in the ratio 0.894/0.106. Additionally, the sample may be used to test the ratio Ni 2p<sub>3/2</sub> 3p to 1.

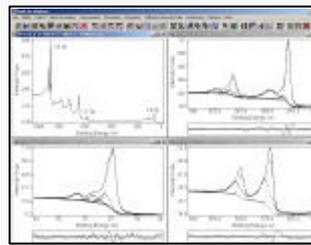


Fig. 4. Estimation of the peak intensities from Ni90Cr10 using peak fit with an adjustable background

**Result:**  
 In case of the quantification from Ni90Cr10 using own estimated transmission functions the deviation from the true value is less than 10% in all studied measurement conditions. In contrast, the deviation is more than 30% using Wagner sensitivity factors.

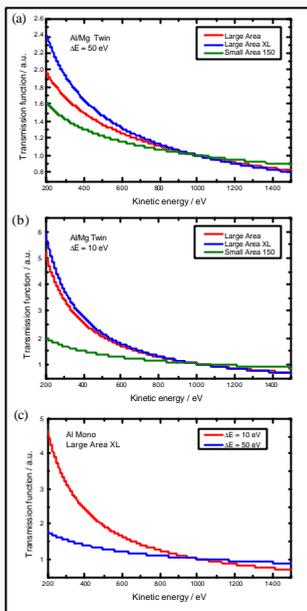


Fig. 3. The estimated transmission functions  $T(E)$  of the spectrometer ESCALAB 220iXL of eight different settings.

### Result:

The variation of the pass energy gives the largest changes of the transmission function  $T(E)$ . The model function

$T(E) = a_0 + b_1 E^{b_2}$  ( $a_0, b_1, b_2$  - parameters) is an appropriate approximation to describe the transmission function.

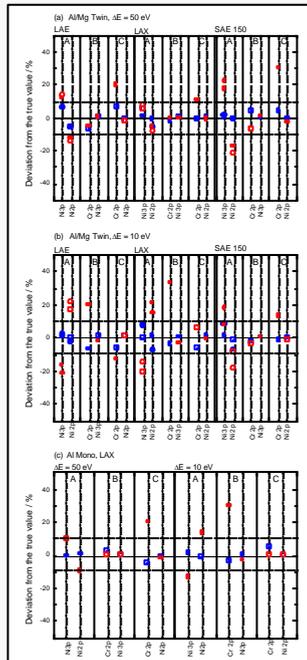


Fig. 5. Comparison of deviations of quantification from Ni90Cr10 using own estimated  $T(E)$  (blue symbols) and Wagner sensitivity factors (red symbols) from the true value. Squares excited by Al Ka, Circle excited by Mg Ka.

## 5. Using UNIFIT 2004

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

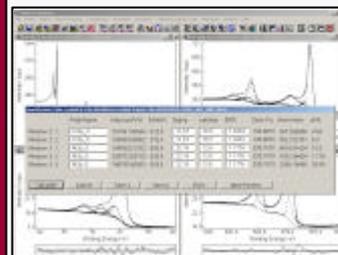


Fig. 6. Dialog window of the element quantification using the product of  $s_i$ ,  $\tau$  and the transmission function  $IEF(T(E))$  as sensitivity factor in UNIFIT 2004. All values can be edited manually.

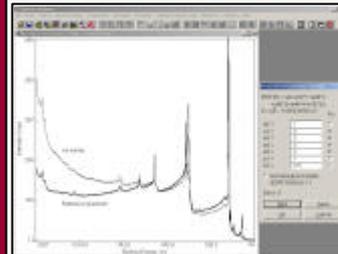


Fig. 7. Survey spectrum of Au, reference spectrum and the dialog to create the model function for the calculation of  $IEF(T(E))$  using the method SSA in UNIFIT 2004.

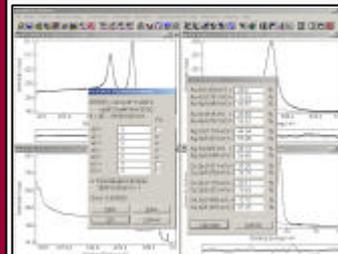


Fig. 8. The left window shows the dialog for the creation of the model function  $IEF(T(E))$  (method QPA). The right window is the input dialog for the normalized intensities  $r_i = I_i / (s_i \cdot I)$  of the standard peaks Au, Ag, Cu and Ge.

## 6. Summary

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

1. estimation of the transmission functions for different spectrometer settings
2. using of  $s$  values of Scofield or Band,
3. using of the recommended  $\tau$  values from the NIST-data base,
4. quantification from relative peak intensities derived from unitted background calculation or peak fits with adjustable background,
5. using the product of  $s_i$ ,  $\tau$  and  $T$  as sensitivity factor.

The new subroutines integrated in the software UNIFIT 2004 allows the estimation of the transmission functions of any XPS spectrometer. The obtained data may be used for the quantification.