

# Improved accuracy of quantitative XPS analysis using predetermined spectrometer transmission functions with UNIFIT 2004

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The accuracy of quantitative XPS analysis can be improved using predetermined transmission functions. Two different calibration methods are used for estimating the transmission function  $T(E)$  of a photoelectron spectrometer, applying a survey spectra approach (SSA) and a quantified peak-area approach (QPA) to minimize the quantification error. For the SSA method, Au, Ag and Cu spectra measured with the Metrology Spectrometer II have been used. The new QPA method was built up 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> standard peak areas, applying adequate ionization cross-sections and mean free path lengths for different pass energies (10 and 50 eV), lens modes (large area, large area XL, small area 150) and x-ray sources (Al/Mg Twin and Al Mono). In the energy range 200–1500 eV a transmission function  $T(E) = a_0 + b_1E^{b_2}$  (where  $a_0$ ,  $b_1$  and  $b_2$  are variable parameters) was found to give an appropriate approximation for eight tested spectrometer settings, implementing the largest changes in the case of pass energy variations. Determination and application of the transmission functions were integrated in the XPS analysis software (UNIFIT 2004) and tested by means of an Ni90Cr10 alloy. The results demonstrate the practicability of the SSA and QPA methods, giving decreased errors of <8% in comparison with errors up to 38% obtained using Wagner's sensitivity factors. Copyright © 2005 John Wiley & Sons, Ltd.

**KEYWORDS:** spectrum analysis software; photoelectron spectroscopy; quantification; transmission function; intensity scale calibration

## INTRODUCTION

One of the aims of x-ray core-level photoelectron spectroscopy (XPS) is investigation of the sample composition.<sup>1</sup> Additionally, angle-resolved XPS (ARXPS) may give information on the depth distribution of elements and their compounds from the first 10 nm. In the case of very thin films the thickness can be estimated also by recording photoelectrons of different kinetic energies from the same element, e.g. Ga 3d and Ga 2p<sub>3/2</sub>.<sup>2</sup> An essential requirement for all these cases of quantitative analysis is a reliable calibration of the intensity scale of the spectrometer used.

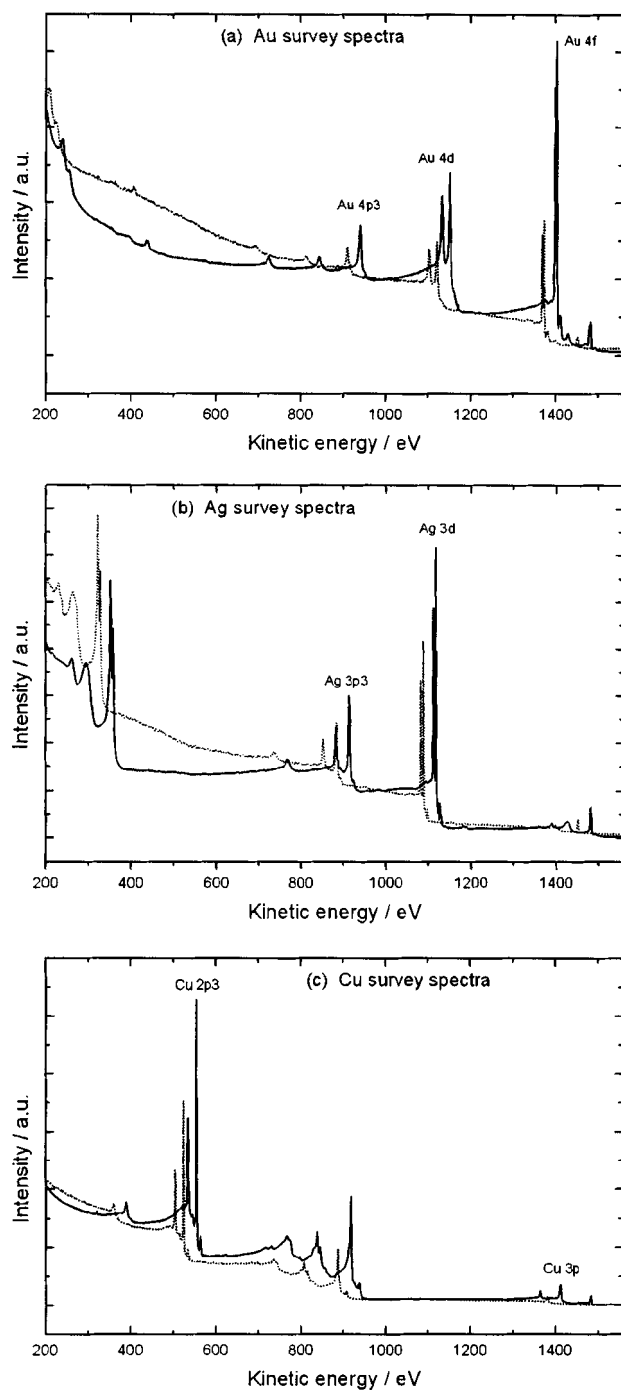
The identification of different chemical species by means of the binding energies of particular peak components requires a well-calibrated energy scale of the spectrometer,<sup>3</sup> as well as a careful analysis of the spectra with appropriate software.<sup>4,5</sup> An accuracy of 0.1 eV seems attainable.

Quantification by peak areas of the analysed chemical species is much more complicated, particularly if an accuracy of better than 10% is demanded. Both the nature of the emission of photoelectrons<sup>1,6</sup> and the development

of spectrometers in the recent 15 years complicate the quantification from XPS data. Without an appropriate calibration of the intensity scale of the spectrometer, quantification errors of >100% are possible.<sup>7</sup>

Because modern XPS spectrometers are equipped with (i) two x-ray sources, one with two anodes Al and Mg (Al/Mg Twin) and another with an Al anode and a monochromator (Al Mono), (ii) a sophisticated lens system consisting of mechanical apertures and electrical and magnetic lenses and (iii) the possibility of a large variation of the pass energy  $\Delta E$ , different intensity/energy response functions (IERFs)<sup>1</sup> may exist in the same spectrometer.<sup>8</sup> Therefore, quantification using relative sensitivity factors from general databases (e.g. Wagner *et al.*<sup>9</sup>) may give poor results (see Fig. 1 and Table 1). In the case of large distances between kinetic energies of the analysed peaks, for example, uncertainties due to different spectrometer settings may increase. The use of theoretical calculations combined with well-estimated IERFs for the spectrometer seems to lead to a higher accuracy of quantification. Using known data for the ionization cross-section  $\sigma$  and the inelastic mean free path  $\lambda$ , the problem is reduced to estimating the IERF given by the product of the analyser transmission function  $T(E)$  and the detector efficiency. By applying a constant analyser

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**Figure 1.** Survey spectra for the reference samples Au (a), Ag (b) and Cu (c) using Al Twin, LAX (lens setting, see Experimental) and different pass energies:  $\Delta E = 50$  eV (straight line) and  $\Delta E = 10$  eV (dotted line). The plot of the spectra are normalized to the intensity  $I(1000 \text{ eV})$ . The spectrum measured with  $\Delta E = 10$  eV is shown with an energy shift of 30 eV.

energy (CAE) mode (constant pass energy  $\Delta E$ ), the detector term can be ignored and estimation of the IERF is reduced to determination of  $T(E)$ . Seah<sup>10</sup> gives a comprehensive theoretical analysis and practical instruction for the absolute calibration of Auger and photoelectron spectrometers.

This work is focused primarily on presenting the practicability and handling of two different methods for determining  $T(E)$ . The use of relative intensities, theoretical

**Table 1.** Quantification of standard spectra of Au, Ag and Cu using Wagner's sensitivity factors<sup>9</sup> with an Escalab 220 iXL spectrometer at two different pass energies: the spectra are shown in Fig. 1 and the true result of quantification from two different peaks of the same element should be 50:50 (setting: Al Twin, LAX)

$\Delta E$ (eV)	Intensity ratio (%)					
	Au 4f	Au 4d <sub>5/2</sub>	Ag 3d	Ag 3p <sub>3/2</sub>	Cu 3p	Cu 2p <sub>3/2</sub>
50	34	66	39	61	56	47
10	33	67	37	63	42	61

well-known  $\sigma$  and  $\lambda$  values and predetermined estimated IERFs should result in a considerably higher accuracy of quantitative analysis from XPS data. Also, the easy handling of newly integrated subroutines in the spectrum analysis software (UNIFIT 2004) is illustrated.

## THEORETICAL BASIS

### Quantification

The intensity ratio  $I_A/I_B$  of photoelectrons of kinetic energies  $E_A$  and  $E_B$  of two pure elements A and B as solid samples is given by<sup>11</sup>

$$\frac{I_A}{I_B} = \frac{N_A \sigma_A \lambda_A(E_A) T(E_A)}{N_B \sigma_B \lambda_B(E_B) T(E_B)} \quad (1)$$

where  $N = N_0 \rho / A$  is the atomic density ( $N_0$  is Avogadro's constant,  $\rho$  is the density of the sample and  $A$  is the relative atomic mass),  $\sigma$  is the ionization cross-section of the observed photoelectron line according to a defined core level and the photon energy  $h\nu$ ,  $\lambda(E)$  is the inelastic mean free path and  $T(E)$  is the transmission function of the spectrometer used.

Equation (1) is defined according to the following assumptions:

- (1) The samples are homogeneous and flat.
- (2) The samples are fine-grained or amorphous, which means that the photoelectrons do not show interference effects.
- (3) The average angle between the incident photons and the analysed photoelectrons is set at the magic angle of  $55^\circ$ .
- (4) The detector efficiency is constant.
- (5) The influence of elastic scattering is negligible.

In the case of a sample consisting of two elements, Eqn. (1) can be written as

$$\frac{I_{(A)}}{I_{(B)}} = \frac{N_{(A)} \sigma_A \lambda_{(A)}(E_A) T(E_A)}{N_{(B)} \sigma_B \lambda_{(B)}(E_B) T(E_B)} \quad (2)$$

where  $I_{(A)}$  and  $I_{(B)}$  are the photoelectron intensities of elements A and B of the alloy sample AB, with

$$N_{(A)} = c_A N_0 \rho_{AB} / \sum_X c_X A_X \quad (3)$$

where  $c_A$  is the atomic fraction of element A and X describes the elements. The difference between the values  $N_{(A)}$  and  $N_A$  or  $\lambda_{(A)}$  and  $\lambda_A$  represents the so-called matrix effect.

With corrected intensity  $I'$  given by

$$I' = \frac{I}{\sigma\lambda(E)T(E)} \quad (4)$$

an approximate estimation of the atomic ratio of elements A and B is obtained by neglecting the matrix effect originating from  $\lambda$

$$\frac{I'_{(A)}}{I'_{(B)}} \approx \frac{c_A}{c_B} \quad (5)$$

The atomic fraction of an element A in a solid sample is then

$$c_A = \frac{I'_A}{\sum_X I'_X} \quad (6)$$

giving unity for the sum of all elements

$$\sum_X c_X = 1 \quad (7)$$

Comparing different photoelectron lines 1... $n$  of one pure element A, all the corrected intensities have to be equal

$$I'_{A1} = I'_{A2} = \dots = I'_{An} \quad (8)$$

and, provided that  $\sigma$  and  $\lambda$  are well-known quantities, Eqn. (8) may be used to calculate and test the transmission function  $T(E)$ .

### Transmission function from survey spectra approach (SSA)

The transmission function  $T$  of a particular spectrometer and spectrometer setting determines the fraction of photoelectrons from the sample reaching the detector as a function of their kinetic energies. Although  $T$  is a function only of  $E$  for older spectrometers equipped with one x-ray anode and without lenses, for new instruments  $T$  depends on four essential setting parameters:

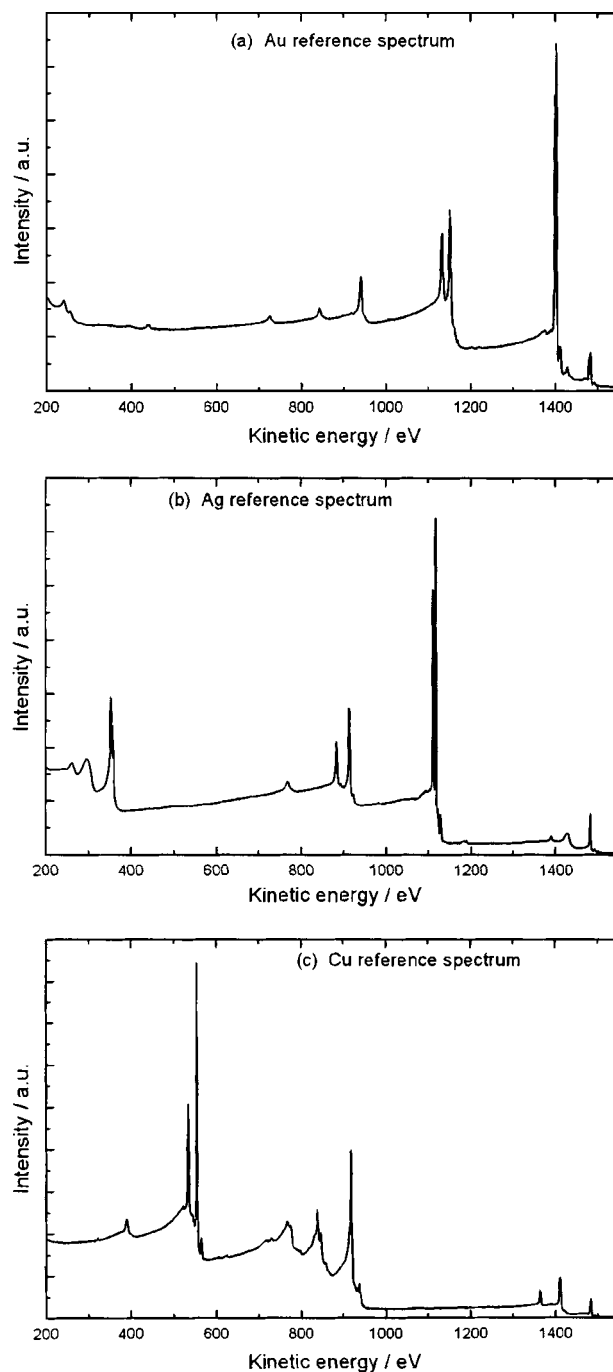
- (1) Kinetic energy  $E$  of photoelectrons.
- (2) Pass energy  $\Delta E$ .
- (3) Lens mode  $L$ .
- (4) X-ray source  $Q$ .

giving  $T(E) \rightarrow T(E, \Delta E, L, Q)$ . Therefore any investigation of the transmission function  $T$  of any spectrometer should account for all the spectrometer settings referred to above.

In order to find the unknown transmission function  $T$  of any spectrometer, Smith and Seah<sup>12</sup>, Seah<sup>10</sup> and Cumpson *et al.*<sup>13</sup> recommend the adaptation of measured survey spectra  $M(E)$  for  $X = \text{Au, Ag or Cu}$  on reference spectra  $S(E)$  recorded for the Metrology Spectrometer II with

$$M_X(E) = T_X(E) \cdot S_X(E) \quad (9)$$

The reference spectra  $S_{\text{Au}}$ ,  $S_{\text{Ag}}$  and  $S_{\text{Cu}}$  derived from the NPL software<sup>14</sup> are shown in Fig. 2. The transmission functions  $T_X(E)$  for the NPL test spectra  $M_{\text{Au}}$ ,  $M_{\text{Ag}}$  and  $M_{\text{Cu}}$  were calculated using the NPL software.<sup>14</sup> Equation (9) gives the reference spectra  $S_X(E)$ . The NPL test spectra were recorded using Al Twin (12 kV, 20 mA) with energy intervals of



**Figure 2.** Reference spectra of Au (a), Ag (b) and Cu (c) generated on the Metrology Spectrometer II of the NPL<sup>14</sup> (Al Twin,  $\Delta E = 50$  eV). All spectra represent measurements of a perfect analyser with a constant transmission function  $T(E) = 1$ .

1 eV and an energy range 200–1560 eV. Cumpson *et al.*<sup>13,14</sup> approximated the transmission function by fitting a rational function of nine parameters.

We applied the same method using a model function consisting of seven parameters

$$T(E) = a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4 + b_1E^{b_2} \quad (10)$$

where  $E$  is the kinetic energy and  $\varepsilon = (E - 1000 \text{ eV})/1000 \text{ eV}$ . All the parameters may be varied or fixed at a certain value.

**Table 2.** The QPA calculation of  $T(E)$  from Eqns (10) and (19): step width and start and end point of the four cycles ( $x_{\min}$  is the optimized parameter after each cycle)

Number of cycle	Parameters					
	$a_0, a_1, a_2, a_3, a_4, b_1$			$b_2$		
	Step width	Start point	End point	Step width	Start point	End point
1	1	5	-5	0.2	0	-2
2	0.1	$x_{\min} + 0.5$	$x_{\min} - 0.5$	0.02	$x_{\min} + 0.1$	$x_{\min} - 0.1$
3	0.01	$x_{\min} + 0.05$	$x_{\min} - 0.05$	0.002	$x_{\min} + 0.01$	$x_{\min} - 0.01$
4	0.001	$x_{\min} + 0.005$	$x_{\min} - 0.005$	0.0002	$x_{\min} + 0.001$	$x_{\min} - 0.001$

Because  $\varepsilon(1000 \text{ eV}) = 0$ , parameters  $a_1$ – $a_4$  do not influence  $T$  at the point  $E = 1000 \text{ eV}$ . The shape of  $T$  most strongly depends on the parameter  $b_2$  varying between  $-0.2$  and  $-2$ . The determination of parameters by minimizing  $\chi^2$  is carried out using the Marquardt–Levenberg algorithm.<sup>15</sup> The same procedure is used already for peak fitting in our software program UNIFIT 2004.<sup>4,5</sup> The quantity of  $\chi^2$  for  $X = \text{Au, Ag}$  or  $\text{Cu}$  can be defined by

$$\chi^2(a_0, a_1, a_2, a_3, a_4, b_1, b_2) = \sum \frac{[S_X(E) \cdot T_X(E, a_0, a_1, a_2, a_3, a_4, b_1, b_2) - M_X(E)]^2}{M_X(E)} \quad (11)$$

A perfect approach should result in identical functions  $T_{\text{Au}}$ ,  $T_{\text{Ag}}$  and  $T_{\text{Cu}}$ . From the average  $T_M$  of the transmission function  $T_X$

$$T_M(E) = \frac{T_{\text{Au}}(E) + T_{\text{Ag}}(E) + T_{\text{Cu}}(E)}{3} \quad (12)$$

Again, by minimizing  $\chi^2$  the final set of parameters is obtained

$$\chi^2(a_0, a_1, a_2, a_3, a_4, b_1, b_2) = \sum \frac{[T(E, a_0, a_1, a_2, a_3, a_4, b_1, b_2) - T_M(E)]^2}{T_M(E)} \quad (13)$$

### Transmission function from the quantified peak-area approach (QPA)

Estimation of the transmission function using the SSA method is not possible in all cases. Internal scattering of the

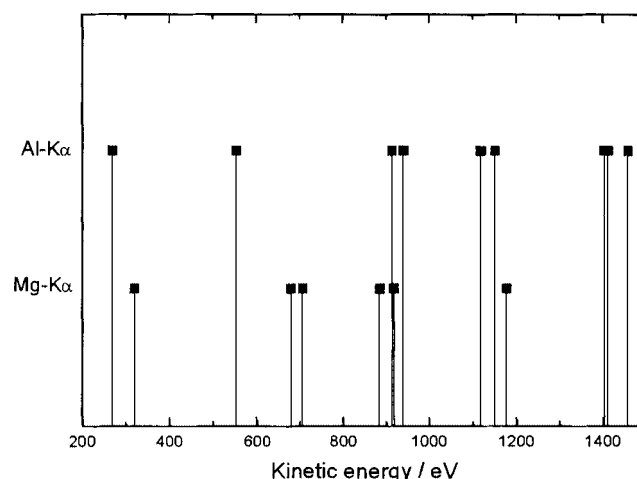
**Table 3.** Parameters of the different lens settings of the Escalab 220 iXL spectrometer: the potentials on lenses L1–L5 result from the product of the lens parameter and the retard potential; parameter C1 of magnetic lens LM describes the current

Lens	Parameters		
	LAE	LAX	SAE 150
L1	0.73	0	-5.05
L2	0.48	-2.6	-2.5
L3a	0	-3.6	0
L3b	0.7	-2.0	-3.5
L3c	0	0	0
L5	0	0	0
LM, C1	0	37.5	0
Field of view	Open	Open	5
Objective iris	Open	Open	7

photoelectrons in the spectrometer may change the spectral background strongly. The examples given by Seah *et al.*<sup>14,16</sup> show that internal scattering becomes important at pass energies  $\Delta E < 20 \text{ eV}$ , therefore the reference spectra recorded for the Metrology Spectrometer II are unsatisfactory for the measured survey spectra obtained using the SSA method. Assuming that the internal scattering influences only the spectral background and not the background-corrected intensities of the peaks, we suggest a new quantified peak-area approach (QPA) to estimate the transmission function of the XPS spectrometer. Seah and Anthony<sup>17</sup> proposed a similar procedure when comparing two different spectrometers.

In order to estimate the transmission function  $T$ , standard spectra 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 3d and Ge 2p<sub>3/2</sub> excited with Al K $\alpha$  and Mg K $\alpha$  radiation were used. The two Ge peaks were added because at the lower energy and monochromatized Al K $\alpha$  excitation the number of available lines of Au, Ag and Cu is insufficient.

Provided that the relative quantification of two photoelectron lines 1 and 2 for a clean surface of pure element A using suitable sensitivity factors and exactly estimated peak intensities  $I$  gives the ratio 1:1, we can determine the transmission function  $T(E)$ . If the sensitivity factor is the product of  $T(E)$ ,  $\sigma(h\nu)$  and  $\lambda(E)$ , and if we assume additionally that the values of  $\sigma(h\nu)$  and  $\lambda(E)$  are well-known, then the ratio  $T(E_{A1})/T(E_{A2})$  can be obtained. Using Eqns (4) and (8) we

**Figure 3.** Energy positions of the standard peaks of Au, Ag, Cu and Ge used for intensity measurements of photoelectrons.

can write

$$\frac{I'_{A1}}{I'_{A2}} = \frac{I_{A1}/[\sigma_{A1}\lambda_{A1}(E_{A1})T(E_{A1})]}{I_{A2}/[\sigma_{A2}\lambda_{A2}(E_{A2})T(E_{A2})]} = 1 \quad (14)$$

and transferring  $T(E_{A1})$  and  $T(E_{A2})$  to the right-hand side of Eqn. (14) gives

$$\frac{I_{A1}/[\sigma_{A1}\lambda_{A1}(E_{A1})]}{I_{A2}/[\sigma_{A2}\lambda_{A2}(E_{A2})]} = \frac{T(E_{A1})}{T(E_{A2})} \quad (15)$$

Introducing the normalized reference ratios  $r_{Ai}$  of the standard peaks

$$r_{Ai} = \frac{I_{Ai}/[\sigma_{Ai} \cdot \lambda_{Ai}(E_{Ai})]}{\sum_{j=1}^n I_{Aj}/[\sigma_{Aj}\lambda_{Aj}(E_{Aj})]} \quad (16)$$

we can write

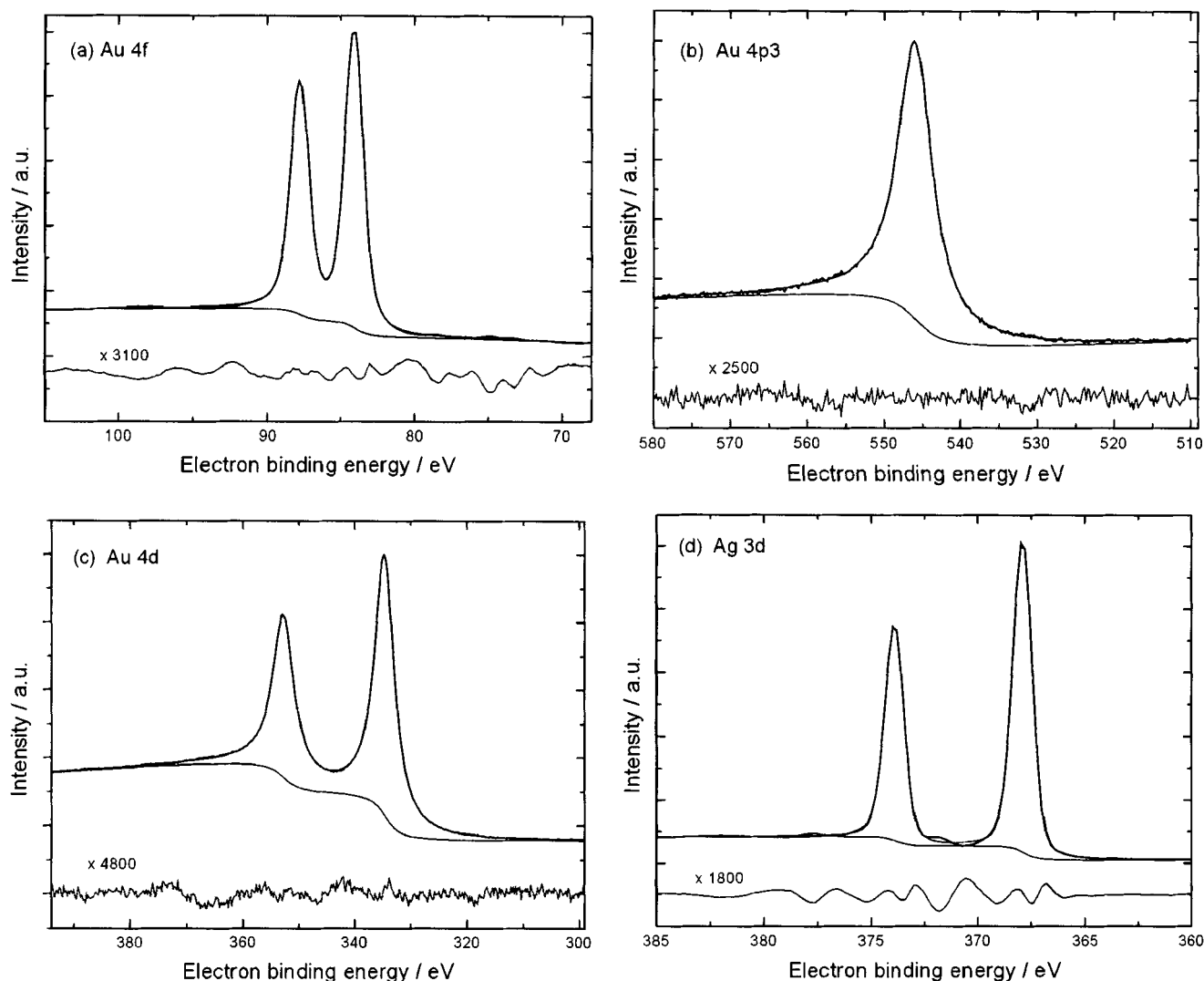
$$\frac{r_{A1}}{r_{A2}} = \frac{T(E_{A1})}{T(E_{A2})} \quad (17)$$

or

$$\frac{T(E_{A2}) \cdot r_{A1}}{T(E_{A1}) \cdot r_{A2}} = 1 \quad (18)$$

The value  $\lambda(E)$  of pure elements can be obtained from the database generated by NIST.<sup>18</sup> For compounds, the TPP-2M equation derived from Tanuma, Penn and Powell<sup>19</sup> can be used but four elementary values are necessary: the number of valence electrons per 'molecule' (for compounds or alloys  $N_v$  is calculated from the sum of the contribution from each constituent element); the density for the compound ( $\text{g cm}^{-3}$ ); the molecular weight ( $M$ ); and the bandgap energy (eV).

The results of Seah *et al.*<sup>8</sup> support the cross-sections of Scofield<sup>20</sup> and Band *et al.*<sup>21</sup> Except for the 4f lines, the values of Band *et al.*<sup>21</sup> were used in our investigations. By comparative studies we found the values  $\sigma_{\text{Au4f}}(1486.6 \text{ eV}) = 14.2$  and  $\sigma_{\text{Au4f}}(1253.6 \text{ eV}) = 16.1$  with the Au 4f lines. All indicated  $\sigma_{Ai}(h\nu)$  values of core levels  $i$  from element A are normalized by  $\sigma_{\text{C1s}}(h\nu)$ .



**Figure 4.** Peak fit of the standard peaks for: (a) Au 4f, (b) Au 4p<sub>3/2</sub>, (c) Au 4d, (d) Ag 3d, (e) Ag 3p, (f) Cu 3p, (g) Cu 2p<sub>3/2</sub>, (h) Ge 3d, (i) Ge 2p<sub>3/2</sub>. The spectra were recorded with an Escalab 220 iXL spectrometer using Al Mono,  $\Delta E = 50 \text{ eV}$  and LAX. Solid lines: (top) spectrum; (middle) background; (bottom) residual.

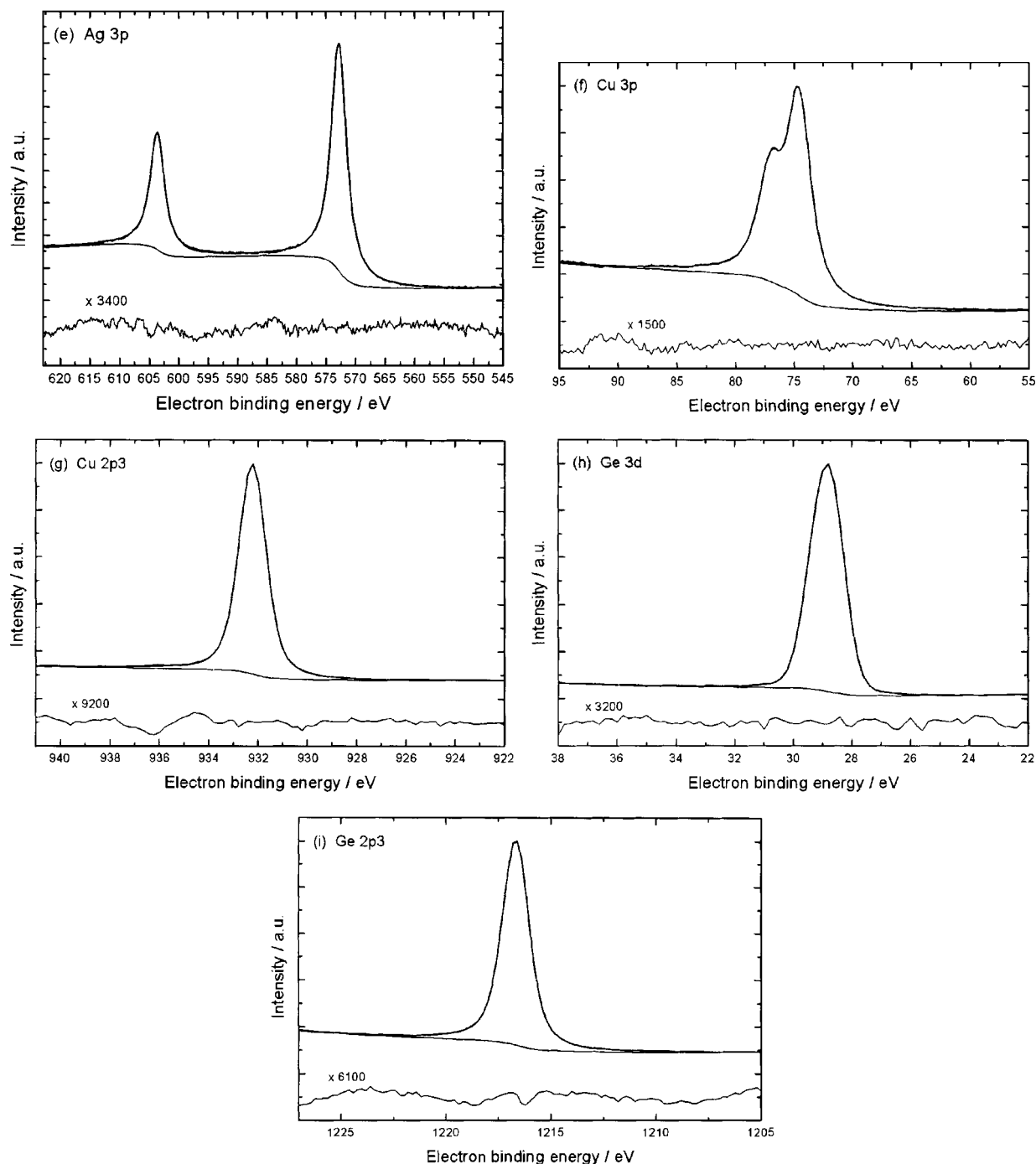


Figure 4. (Continued).

After calculating the reference ratios  $r_i$  (Eqn (16)) with Eqn (18) for all standard samples, the transmission function  $T(E)$  may be approximated by minimizing the sum of the squared standard deviations (SSD) by varying the parameters of the selected model function  $T(E)$  from Eqn. (10)

$$\begin{aligned}
 SSD = & \left[ \frac{T(1143) \cdot r_{\text{Au}4f}(1401)}{T(1401) \cdot r_{\text{Au}4d}(1143)} - 1 \right]^2 \\
 & + \left[ \frac{T(940) \cdot r_{\text{Au}4f}(1401)}{T(1401) \cdot r_{\text{Au}4p^3}(940)} - 1 \right]^2 \\
 & + \left[ \frac{T(1143) \cdot r_{\text{Au}4p^3}(940)}{T(940) \cdot r_{\text{Au}4d}(1143)} - 1 \right]^2
 \end{aligned}$$

$$\begin{aligned}
 & + \left[ \frac{T(1411) \cdot r_{\text{Cu}2p^3}(554)}{T(554) \cdot r_{\text{Cu}3p}(1411)} - 1 \right]^2 \\
 & + \left[ \frac{T(1116) \cdot r_{\text{Ag}3p^3}(914)}{T(914) \cdot r_{\text{Ag}3d}(1116)} - 1 \right]^2 \\
 & + \left[ \frac{T(1457) \cdot r_{\text{Ge}2p^3}(270)}{T(270) \cdot r_{\text{Ge}3d}(1457)} - 1 \right]^2 \\
 & + \left[ \frac{T(910) \cdot r_{\text{Au}4p^3}(707)}{T(707) \cdot r_{\text{Au}4d}(910)} - 1 \right]^2 \\
 & + \left[ \frac{T(1178) \cdot r_{\text{Cu}2p^3}(321)}{T(321) \cdot r_{\text{Cu}3p}(1178)} - 1 \right]^2
 \end{aligned} \quad (19)$$

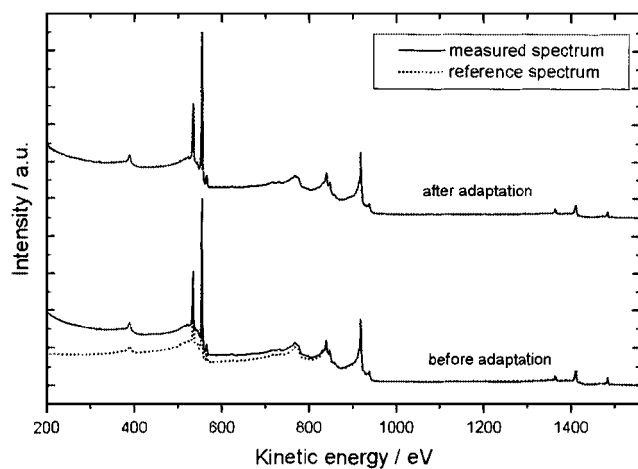
$$+ \left[ \frac{T(883) \cdot r_{\text{Ag}3\text{p}^3}(681)}{T(681) \cdot r_{\text{Ag}3\text{d}}(883)} - 1 \right]^2$$

The kinetic energies were estimated by peak fitting. If a complete doublet is used, the value of the kinetic energy in Eqn. (19) is the arithmetic mean of both lines. The last three terms arise only for Al/Mg Twin excitation, but not for Al Mono.

In order to find the minimum SSD, all possible combinations of the free parameters of Eqn. (10) were optimized in four cycles. The step width and the start and end energies were determined (see Table 2), giving accuracies of 0.001 for parameters  $a_0$ – $b_1$  and 0.0002 for parameter  $b_2$ .

## EXPERIMENTAL

The measurements presented are recorded by means of a VG Escalab 220 iXL spectrometer equipped with a model 220 analyser and a set of six channel electron multipliers with a multidetector dead time of 16 ns. With this system, counting rates up to  $6 \text{ Mc s}^{-1}$  may be used, with linearity better than 1%. In practice, counting rates were kept below  $5 \text{ Mc s}^{-1}$ . The  $180^\circ$  analyser is equipped with one magnetic lens, six electrostatic lenses and two mechanical apertures. Eight different lens settings are available, correlating with the appropriate lens parameters. The parameters of the electrostatic lenses represent the ratio of the lens potential



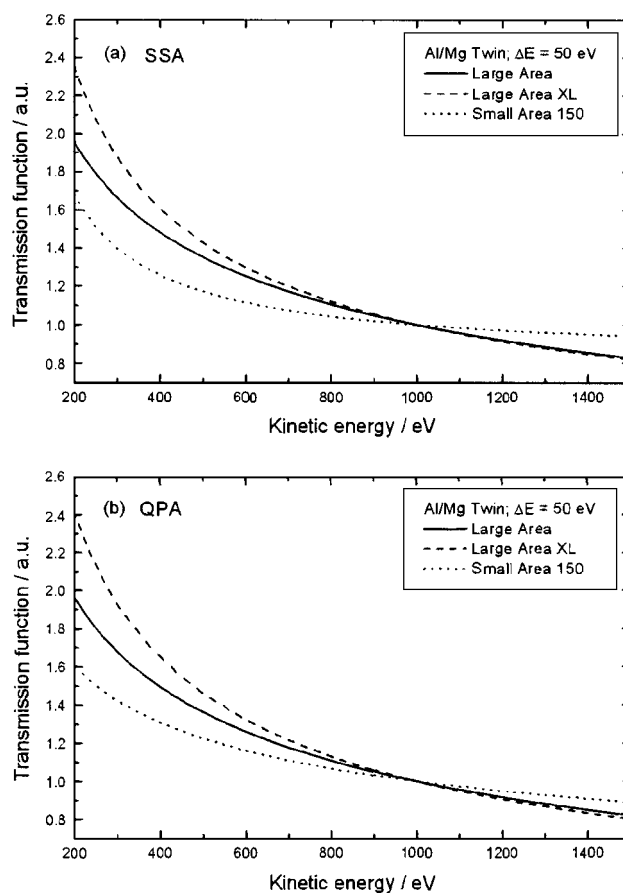
**Figure 5.** Example of successful SSA adaptation of a reference spectrum of copper (dotted line) to a measured spectrum (straight line) by variation of the transmission function  $T(E)$ . Setting: Al Twin,  $\Delta E = 50 \text{ eV}$ , LAX.

**Table 4.** Comparison of the  $T(E)$  functions (Eqn. (22)), using SSA with Eqn. (13) and QPA with Eqn. (19): the parameters are normalized to  $T(1000 \text{ eV}) = 1$  (setting: Al Twin,  $\Delta E = 50 \text{ eV}$ )

Lens	Parameters					
	SSA			QPA		
	$a_0$	$b_1$	$b_2$	$a_0$	$b_1$	$b_2$
LAE	-0.4098	13.0176	-0.3218	-0.6361	12.0452	-0.2890
LAX	0.1759	53.4852	-0.6041	0	44.1774	-0.5484
SAE 150	0.8261	163.8471	-0.9914	0.0637	8.0244	-0.3110

to the retarding potential. The values of the three studied lens settings LAE (large area), LAX (large area with magnetic lens XL) and SAE 150 (small area  $150 \mu\text{m}$ ) are summarized in Table 3. The combination of these three lens settings with two pass energies ( $\Delta E = 50$  and  $10 \text{ eV}$ ) and two x-ray sources (Al/Mg Twin and Al Mono) gives a set of 12 different spectrometer settings; only eight spectrometer settings were investigated because measurements with the Al Mono source were carried out using only the lens setting LAX.

For survey scans we use the pass energy  $\Delta E = 50 \text{ eV}$ . Narrow scans are measured using  $\Delta E = 10 \text{ eV}$ . For large samples ( $10 \times 10 \text{ mm}$ ) the Escalab 220i XL spectrometer has the best intensity with the Al/Mg Twin anode and the lens setting LAE. To measure small samples with high intensity and excellent energy resolution, the best lens setting is LAX combined with Al Mono excitation. A huge intensity is achieved by placing a magnetic lens under the sample, which generates a wide acceptance angle for the emitted electrons. For angle-resolved XPS, the lens setting LAX is completely inappropriate. Measurements with a mandatory small-angle acceptance (e.g. forward-scattering x-ray photoelectron diffraction, XPD) are recorded using the Al/Mg Twin anode and lens setting SAE 150. Additionally, two mechanical apertures were set to 7 for the objective lens and 5 for the field



**Figure 6.** The optimized transmission functions  $T(E)$  (Eqn. (22)) of three different lens settings using the two different methods: SSA (a) and QPA (b). The functions  $T(E)$  are normalized to  $T(1000 \text{ eV}) = 1$ . Settings: Al/Mg Twin;  $\Delta E = 50 \text{ eV}$ ; LAE, LAX and SAE 150.

**Table 5(a).** Testing results of the SSA method (setting: Al/Mg Twin,  $\Delta E = 50$  eV, LAE)

X-ray source	Line $A_i$	$E$ (eV)	$\frac{I_{A_i}}{\sum_j I_{A_j}}$	$\sigma_{A_i}$	$\frac{I_{A_i}/\sigma_{A_i}}{\sum_j I_{A_j}/\sigma_{A_j}}$	$\lambda_{A_i}(E)$ (Å)	$r_{A_i}$	SSA results			Results after Wagner		
								$T(E_{A_i})$	$\frac{r_{A_i}/T(E_{A_i})}{\sum_j r_{A_j}/T(E_{A_j})}$	Error (%)	$SF_{A_i}$	$\frac{I_{A_i}/SF_{A_i}}{\sum_j I_{A_j}/SF_{A_j}}$	Error (%)
Al $K\alpha$	Au 4f	1401	0.3673	14.2	0.3509	17.79	0.3010	0.855	0.336	-0.6	—	—	—
	Au 4d	1143	0.4976	19.9	0.3392	15.23	0.3399	0.981	0.331	+0.4	—	—	—
	Au 4p <sub>3/2</sub>	940	0.1351	5.92	0.3096	13.16	0.3591	1.028	0.333	0	—	—	—
Mg $K\alpha$	Au 4d	910	0.7923	16.1	0.5199	12.83	0.4741	1.043	0.502	+0.4	—	—	—
	Au 4p <sub>3/2</sub>	707	0.2077	4.57	0.4801	10.68	0.5259	1.166	0.498	-0.4	—	—	—
Al $K\alpha$	Ag 3d	1116	0.6913	18.0	0.5016	16.22	0.4636	0.951	0.486	-2.8	5.20	0.396	-20.8
	Ag 3p <sub>3/2</sub>	914	0.3087	8.09	0.4984	13.93	0.5364	1.041	0.514	+2.8	1.52	0.604	+20.8
Mg $K\alpha$	Ag 3d	883	0.7324	18.1	0.5033	13.57	0.4550	1.058	0.484	-3.2	5.20	0.445	-11.0
	Ag 3p <sub>3/2</sub>	681	0.2676	6.7	0.4967	11.18	0.5450	1.186	0.516	+3.2	1.52	0.555	+11.0
Al $K\alpha$	Cu 3p	1411	0.1618	2.49	0.5657	21.46	0.3942	0.852	0.497	-0.6	0.65	0.555	+11.0
	Cu 2p <sub>3/2</sub>	554	0.8382	16.8	0.4343	10.72	0.6058	1.295	0.503	+0.6	4.2	0.445	-11.0
Mg $K\alpha$	Cu 3p	1178	0.1770	2.30	0.6009	18.65	0.3796	0.928	0.517	+3.4	0.65	0.582	+16.4
	Cu 2p <sub>3/2</sub>	321	0.8230	16.1	0.3991	7.58	0.6204	1.623	0.483	-3.4	4.2	0.418	-16.4
Al $K\alpha$	Ge 3d	1457	0.0790	1.41	0.5945	28.38	0.3071	0.839	0.479	-4.2	0.38	0.579	+15.8
	Ge 2p <sub>3/2</sub>	270	0.9210	24.1	0.4055	8.58	0.6929	1.740	0.521	+4.2	6.10	0.421	-15.8

Energy and intensity data for 15 standard peaks used to test the transmission function  $T(E)$  (column 9). The normalized intensity ratios using Eqn. (6) are shown in column 10. In order to compare the results, column 13 presents the quantification using Wagner's sensitivity factors ( $SF$ ).<sup>9</sup> The uncertainties of both methods are presented in columns 11 and 14 (see also Fig. 7(a), LAE). The stepwise correction of the intensity is shown in column 4 (without correction), column 6 (correction only with  $\sigma$ ) and column 8 (correction with  $\sigma$  and  $\lambda$ , Eqn. (16)).

**Table 5(b).** Testing results of the SSA method (setting: Al/Mg Twin,  $\Delta E = 50$  eV, LAX and SAE 150)

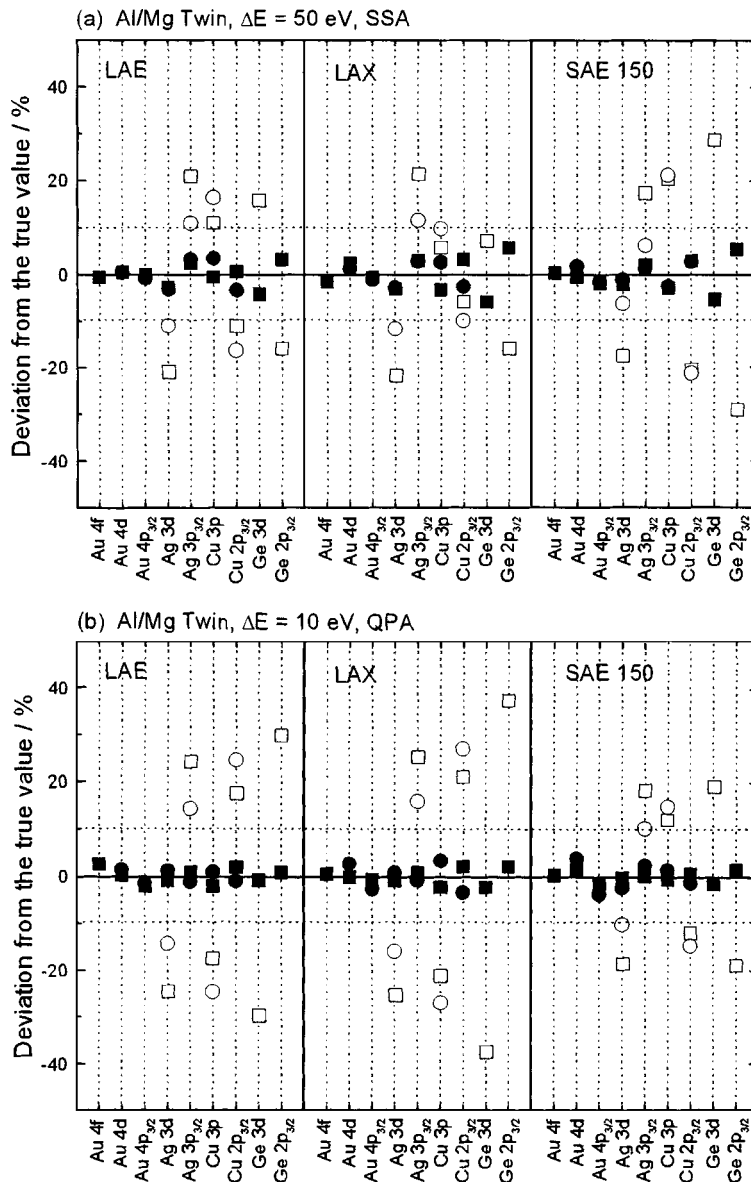
X-ray source	Line $A_i$	$E$ (eV)	LAX				SAE 150			
			SSA results		Results after Wagner		SSA results		Results after Wagner	
			Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Al $K\alpha$	Au 4f	1401	0.328	-1.5	—	—	0.334	+0.3	—	—
	Au 4d	1143	0.341	+2.4	—	—	0.331	-0.6	—	—
	Au 4p <sub>3/2</sub>	940	0.331	-0.5	—	—	0.327	-1.8	—	—
Mg $K\alpha$	Au 4d	910	0.504	+0.9	—	—	0.506	+1.2	—	—
	Au 4p <sub>3/2</sub>	707	0.496	-0.9	—	—	0.494	-1.2	—	—
Al $K\alpha$	Ag 3d	1116	0.485	-3.0	0.392	-21.5	0.490	-2.0	0.412	-17.6
	Ag 3p <sub>3/2</sub>	914	0.515	+3.0	0.608	+21.5	0.510	+2.0	0.588	+17.6
Mg $K\alpha$	Ag 3d	883	0.486	-2.9	0.442	-11.5	0.494	-1.2	0.469	-6.2
	Ag 3p <sub>3/2</sub>	681	0.514	+2.9	0.558	+11.5	0.506	+1.2	0.531	+6.2
Al $K\alpha$	Cu 3p	1411	0.484	-3.2	0.529	+5.9	0.486	-2.8	0.602	+20.4
	Cu 2p <sub>3/2</sub>	554	0.516	+3.2	0.471	-5.9	0.514	+2.8	0.398	-20.4
Mg $K\alpha$	Cu 3p	1178	0.513	+2.5	0.549	+9.9	0.487	-2.6	0.606	+21.2
	Cu 2p <sub>3/2</sub>	321	0.487	-2.5	0.451	-9.9	0.513	+2.6	0.394	-21.2
Al $K\alpha$	Ge 3d	1457	0.471	-5.9	0.536	+7.2	0.473	-5.4	0.644	+28.8
	Ge 2p <sub>3/2</sub>	270	0.529	+5.9	0.464	-7.2	0.527	+5.4	0.356	-28.8

Energy and intensity data for 15 standard peaks used to test the transmission function  $T(E)$ . The determined test ratios (cf. Eqn. (6)) are present in columns 4 and 8. The results of quantification using Wagner's sensitivity factors ( $SF$ )<sup>9</sup> are expressed in columns 6 and 10. The uncertainties of both methods are presented in columns 5, 7, 9 and 11 (see also Fig. 7(a), LAX and SAE 150).

of view. For this special spectrometer setting, we estimated an angle acceptance of  $\sim 4^\circ$  and a spot diameter of  $\sim 2$  mm.

In this work, the energy scale was calibrated to  $\pm 0.02$  eV (ISO 15472),<sup>3</sup> the instrument was operated in the CAE mode

(constant  $\Delta E$ ) at pass energies of 50 and 10 eV and the angles of the x-ray sources with respect to the surface normal were  $55^\circ$  for the Al/Mg Twin anode and  $58^\circ$  for the Al Mono anode. The base pressure during all experiments was  $5 \times 10^{-10}$  mbar.

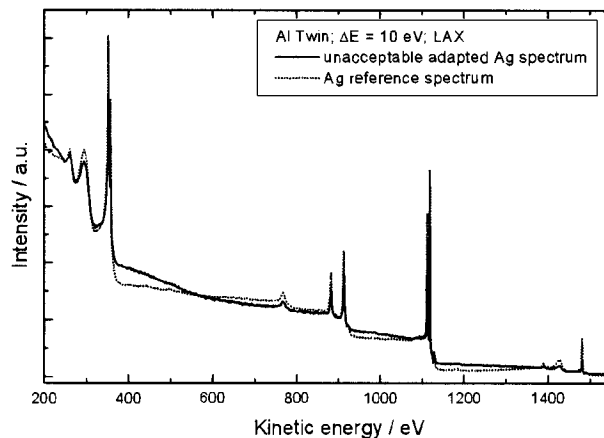


**Figure 7.** Comparison of deviations from the values of 0.33 (for three peaks) and 0.5 (for two peaks) of the quantification results (Eqn. (6)) obtained using the transmission functions  $T(E)$  (full symbols) and Wagner's sensitivity factors<sup>9</sup> (open symbols). Settings: Al Twin (squares) and Mg Twin (circles); LAE, LAX and SAE 150. (a) The SSA transmission function,  $\Delta E = 50$  eV (see Tables 5(a) and 5(b)). (b) The QPA transmission function,  $\Delta E = 10$  eV (see Tables 6(a) and 6(b)).

The samples Au, Ag and Cu were metallic foils and the Ge sample was a clean polished crystal of size  $\sim 12 \times 12$  mm<sup>2</sup>. To remove contamination and to amorphize Ge, the samples were sputtered using 3–5 keV argon ions. After sputtering, the C 1s peak in the survey spectra was observed below the noise level. An XPD experiment carried out on Ge showed no forward-scattering effects.

The surveys for the SSA method were recorded using the following proposed acquisition conditions:<sup>14</sup> pass energy  $\Delta E = 50$  eV, energy interval = 1 eV, start energy = 1560 eV, end energy = 200 eV, x-ray source was the Al Twin anode with 12 keV, the number of scans was 2 and the dwell time was 300 ms.

Measurements for estimating the function  $T(E)$  using the QPA method were carried out for all 12 different spectrometer settings. The step width of the narrow scans was 0.2 eV for  $\Delta E = 50$  eV and 0.1 eV for  $\Delta E = 10$  eV. The



**Figure 8.** Example of an unacceptable SSA adaptation of a reference spectrum (dotted line) to an Ag survey spectrum (straight line). Setting: Al Twin,  $\Delta E = 10$  eV, LAX.

**Table 6(a).** Testing results of the QPA method (setting: Al/Mg Twin,  $\Delta E = 10$  eV, LAE)

X-ray source	Line $A_i$	$E$ (eV)	$\frac{I_{A_i}}{\sum_j I_{A_j}}$	$\sigma_{A_i}$	$\frac{I_{A_i}/\sigma_{A_i}}{\sum_j I_{A_j}/\sigma_{A_j}}$	$\lambda_{A_i}(E)$ (Å)	$r_{A_i}$	QPA results			Results after Wagner		
								$T(E_{A_i})$	$\frac{r_{A_i}/T(E_{A_i})}{\sum_j r_{A_j}/T(E_{A_j})}$	Error (%)	$SF_{A_i}$	$\frac{I_{A_i}/SF_{A_i}}{\sum_j I_{A_j}/SF_{A_j}}$	Error (%)
Al $K\alpha$	Au 4f	1401	0.3474	14.2	0.3238	17.79	0.2748	0.707	0.342	+2.7	—	—	—
	Au 4d	1143	0.4984	19.9	0.3315	15.23	0.3287	0.871	0.332	-0.3	—	—	—
	Au 4p <sub>3/2</sub>	940	0.1542	5.92	0.3447	13.16	0.3955	1.066	0.326	-2.1	—	—	—
Mg $K\alpha$	Au 4d	910	0.7705	16.1	0.4879	12.83	0.4423	1.102	0.507	+1.4	—	—	—
	Au 4p <sub>3/2</sub>	707	0.2295	4.57	0.5121	10.68	0.5577	1.429	0.493	-1.4	—	—	—
Al $K\alpha$	Ag 3d	1116	0.6749	18.0	0.4827	16.22	0.4449	0.893	0.496	-0.8	5.20	0.378	-24.4
	Ag 3p <sub>3/2</sub>	914	0.3251	8.09	0.5173	13.93	0.5551	1.097	0.504	+0.8	1.52	0.622	+24.4
Mg $K\alpha$	Ag 3d	883	0.7198	18.1	0.4874	13.57	0.4393	1.137	0.506	+1.2	5.20	0.429	-14.2
	Ag 3p <sub>3/2</sub>	681	0.2802	6.7	0.5126	11.18	0.5607	1.485	0.494	-1.2	1.52	0.571	+14.2
Al $K\alpha$	Cu 3p	1411	0.0981	2.49	0.4233	21.46	0.2683	0.701	0.490	-2.0	0.65	0.413	-17.4
	Cu 2p <sub>3/2</sub>	554	0.9019	16.8	0.5767	10.72	0.7317	1.837	0.510	+2.0	4.2	0.587	+17.4
Mg $K\alpha$	Cu 3p	1178	0.0859	2.30	0.3968	18.65	0.2109	0.845	0.505	+1.0	0.65	0.378	-24.4
	Cu 2p <sub>3/2</sub>	321	0.9141	16.1	0.6032	7.58	0.7891	3.222	0.495	-1.0	4.2	0.622	+24.4
Al $K\alpha$	Ge 3d	1457	0.0324	1.41	0.3640	28.38	0.1475	0.679	0.496	-0.8	0.38	0.350	-30.0
	Ge 2p <sub>3/2</sub>	270	0.9676	24.1	0.6360	8.58	0.8525	3.850	0.504	+0.8	6.1	0.650	+30.0

Energy and intensity data for 15 standard peaks used to test the transmission function  $T(E)$  (column 9). The normalized intensity ratios using Eqn. (6) are shown in column 10. In order to compare the results, column 13 presents the quantification using Wagner's sensitivity factors ( $SF$ ).<sup>9</sup> The uncertainties of both methods are presented in columns 11 and 14 (see also Fig. 7(b), LAE). The stepwise correction of the intensity is shown in column 4 (without correction), column 6 (correction only with  $\sigma$ ) and column 8 (correction with  $\sigma$  and  $\lambda$  (Eqn. (16))).

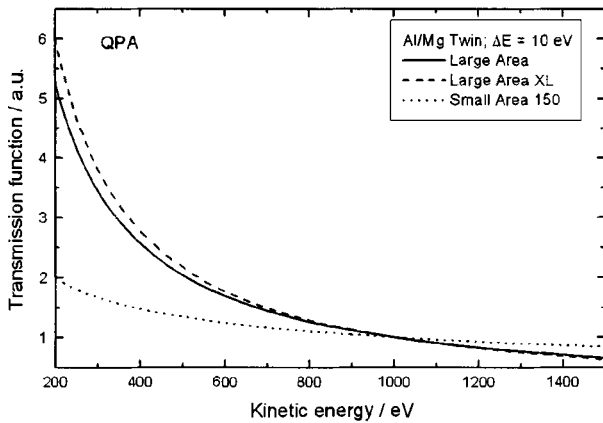
**Table 6(b).** Testing results of the QPA method (setting: Al/Mg Twin,  $\Delta E = 10$  eV, LAX and SAE 150)

X-ray source	Line $A_i$	$E$ (eV)	LAX				SAE 150			
			QPA results		Results after Wagner		QPA results		Results after Wagner	
			Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Al $K\alpha$	Au 4f	1401	0.335	+0.6	—	—	0.334	+0.3	—	—
	Au 4d	1143	0.333	0	—	—	0.338	+1.5	—	—
	Au 4p <sub>3/2</sub>	940	0.332	-0.2	—	—	0.328	-1.5	—	—
Mg $K\alpha$	Au 4d	910	0.509	+1.8	—	—	0.519	+3.8	—	—
	Au 4p <sub>3/2</sub>	707	0.491	-1.8	—	—	0.481	-3.8	—	—
Al $K\alpha$	Ag 3d	1116	0.496	-0.8	0.373	-25.4	0.499	-0.2	0.408	-18.4
	Ag 3p <sub>3/2</sub>	914	0.504	+0.8	0.627	+25.4	0.501	+0.2	0.592	+18.4
Mg $K\alpha$	Ag 3d	883	0.504	+0.8	0.421	-15.8	0.488	-2.4	0.449	-10.2
	Ag 3p <sub>3/2</sub>	681	0.496	-0.8	0.579	+15.8	0.512	+2.4	0.551	+10.2
Al $K\alpha$	Cu 3p	1411	0.489	-2.2	0.394	-21.2	0.497	-0.6	0.560	+12.0
	Cu 2p <sub>3/2</sub>	554	0.511	+2.2	0.606	+21.2	0.503	+0.6	0.440	-12.0
Mg $K\alpha$	Cu 3p	1178	0.517	+3.4	0.364	-27.2	0.507	+1.4	0.574	+14.8
	Cu 2p <sub>3/2</sub>	321	0.483	-3.4	0.636	+27.2	0.493	-1.4	0.426	-14.8
Al $K\alpha$	Ge 3d	1457	0.489	-2.2	0.312	-37.6	0.492	-1.6	0.595	+19.0
	Ge 2p <sub>3/2</sub>	270	0.511	+2.2	0.688	+37.6	0.508	+1.6	0.405	-19.0

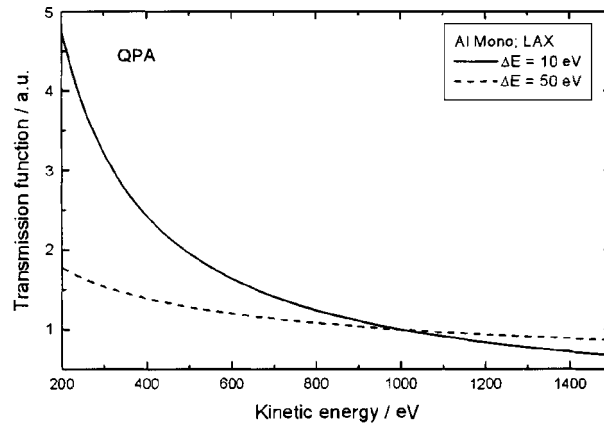
Energy and intensity data for 15 standard peaks used to test the transmission function  $T(E)$ . The determined test ratios (cf. Eqn. (6)) are present in columns 4 and 8. The results of quantification using Wagner's sensitivity factors ( $SF$ )<sup>9</sup> are expressed in columns 6 and 10. The uncertainties of both methods are presented in columns 5, 7, 9 and 11 (see also Fig. 7(b), LAX and SAE 150).

number of scans varied between 3 and 5, but was equal for different spectra of an experiment. The dwell time of each experiment was set to 300 ms. In order to minimize the time-drift error of the intensity, all measurements

were performed using the 'Multiplex scanning' acquisition mode. The energies of the selected spectra are illustrated in Fig. 3. All reference intensities of the standard peaks were determined using three independent experiments.



**Figure 9.** The QPA transmission functions  $T(E)$  (Eqn. (22)) of different lens modes LAE, LAX and SAE 150 and the spectrometer setting of Al/Mg Twin and  $\Delta E = 10$  eV.

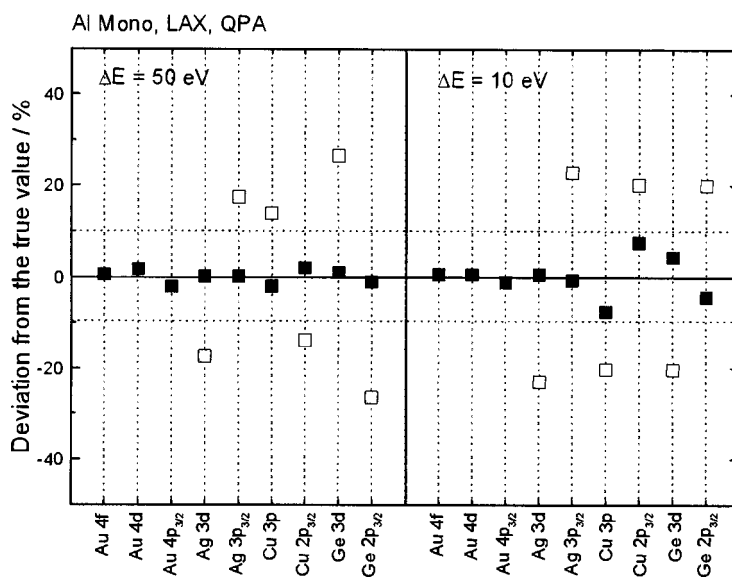


**Figure 10.** The QPA transmission functions  $T(E)$  (Eqn. (22)) of two different pass energies  $\Delta E = 50$  eV and  $\Delta E = 10$  eV and the spectrometer setting of Al Mono and LAX.

**Table 7.** Testing results of the QPA method (setting: Al Mono,  $\Delta E = 50$  and  $10$  eV, LAX)

Line $A_i$	$E$ (eV)	$\Delta E = 50$ eV				$\Delta E = 10$ eV			
		QPA results		Results after Wagner		QPA results		Results after Wagner	
		Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Au 4f	1401	0.335	+0.6	—	—	0.335	+0.6	—	—
Au 4d	1143	0.339	+1.8	—	—	0.336	+0.9	—	—
Au 4p <sub>3/2</sub>	940	0.326	-2.1	—	—	0.329	-1.2	—	—
Ag 3d	1116	0.501	+0.2	0.413	-17.4	0.503	+0.6	0.386	-22.8
Ag 3p <sub>3/2</sub>	914	0.499	-0.2	0.587	+17.4	0.497	-0.6	0.614	+22.8
Cu 3p	1411	0.490	-2.0	0.569	+13.8	0.462	-7.4	0.399	-20.2
Cu 2p <sub>3/2</sub>	554	0.510	+2.0	0.431	-13.8	0.538	+7.4	0.601	+20.2
Ge 3d	1457	0.504	+0.8	0.633	+26.5	0.522	+4.4	0.399	-20.2
Ge 2p <sub>3/2</sub>	270	0.496	-0.8	0.367	-26.5	0.478	-4.4	0.601	+20.2

Energy and intensity data for nine standard peaks used to test the transmission function  $T(E)$ . The determined test ratios (cf. Eqn. (6)) are present in columns 3 and 7. The results of quantification using Wagner's sensitivity factors ( $SF$ )<sup>9</sup> are expressed in columns 5 and 9. The uncertainties of both methods are presented in columns 4, 6, 8 and 10 (see also Fig. 11).



**Figure 11.** Comparison of the deviation from the true values of 0.33 (for three peaks) and 0.5 (for two peaks) of the quantification results obtained using the estimated transmission functions  $T(E)$  (full symbols, Eqn. (6)) and Wagner's sensitivity factors<sup>9</sup> (open symbols). The results of the investigation with the source Al Mono, two pass energies  $\Delta E = 50$  eV and  $10$  eV and lens mode LAX are presented. The function  $T(E)$  was determined using QPA.

**Table 8.** Summary of all estimated parameters of the QPA model function  $T(E)$  (Eqn. (22)) of the different settings: the parameters are normalised to  $T(1000 \text{ eV}) = 1$ 

Lens	Parameters											
	Al/Mg Twin						Al Mono					
	$\Delta E = 50 \text{ eV}$			$\Delta E = 10 \text{ eV}$			$\Delta E = 50 \text{ eV}$			$\Delta E = 10 \text{ eV}$		
	$a_0$	$b_1$	$b_2$	$a_0$	$b_1$	$b_2$	$a_0$	$b_1$	$b_2$	$a_0$	$b_1$	$b_2$
LAE	-0.6361	12.0452	-0.2890	0	1226.87	-1.0296	—	—	—	—	—	—
LAX	0	44.1774	-0.5484	0	2194.87	-1.1138	-0.0035	11.8177	-0.3577	0	798.36	-0.9674
SAE 150	0.0637	8.0244	-0.3110	0.0049	19.0041	-0.4270	—	—	—	—	—	—

The spectrometer settings of Al Twin and  $\Delta E = 50 \text{ eV}$  can be used to compare the SSA and QPA methods.

### PEAK AREA ESTIMATION

The intensities  $I_{xi}$  of the standard peaks were determined using the program UNIFIT 2004<sup>4,5</sup> by convoluting independent Gaussian (G) and Lorentzian (L) contributions resulting in the so-called Voigt profile  $f(E)$

$$f(E) = f(L \times G) = \int_{-\infty}^{\infty} L(E)G(E - E') dE' \quad (20)$$

The fitting parameters, such as peak height, peak position and full width at half-maximum (FWHM), for the Gaussian and Lorentzian contributions were set free. The asymmetry parameter was kept at zero. The spectral background  $B(E)$  was described using the following function

$$B(E) = a + bE + cE^2 + d \cdot \text{Shirley}(E) \quad (21)$$

where  $E$  is the kinetic energy and  $a$ ,  $b$ ,  $c$  and  $d$  are fitting parameters.  $\text{Shirley}(E)$  represents the Shirley background. These four parameters were calculated iteratively during the peak fit.

Alternatively, Seah<sup>3</sup> recommends a Tougaard background approximation to account for inelastic scattering contributions but this requires an energy range of  $>60 \text{ eV}$ . Because we used relative peak areas, we assumed that the relative portion of the inelastic scattered electrons of considered spectra is approximately the same. Figure 4 illustrates the results of the standard peak fit for spectra recorded with the Escalab 220 iXL (monochromatized Al  $K\alpha$  radiation,  $\Delta E = 50 \text{ eV}$ , LAX) and applying the iteratively calculated background  $B(E)$  from Eqn. (21). Even for Ge spectra exhibiting a strong loss structure, acceptable results were obtained. Nevertheless, the quantification of real sample spectra should include as many components as possible from inelastic scattered electrons and shake-up processes.

The excellent agreement between the quantification results of the SSA and QPA methods using the background from Eqn. (21) and reduced scan regions of 15–50 eV confirms the reliability of our approach.

### CALCULATING THE TRANSMISSION FUNCTION

The best analytical description of the transmission function for modern spectrometers tuned to gain maximum intensity

and the highest energetic resolution has not been found. Different ways to apply Eqn. (10) may generate different forms of model functions, depending on the variable parameters. In this paper we applied the formula

$$T(E) = a_0 + b_1 E^{b_2} \quad (22)$$

to approximate the transmission function in all studied cases. Experience shows that the values for  $b_2$  can be expected to be between  $-0.1$  and  $-2$ . This model function is similar to that known from older spectrometers<sup>22</sup>

$$IERF \propto E^{-0.5} \quad (23)$$

and this relation is valid for energies in the medium region (i.e. 500–1500 eV).

The calculation of  $T(E)$  using the **SSA method** described above gives excellent results for all three lens modes and 50 eV pass energy when exciting with a conventional Al  $K\alpha$  Twin source. Figure 5 shows an example of optimal adaptation of the respective reference spectra  $S(E)$  to the measured survey spectra of Cu by varying the parameter of the model function  $T_{Cu}(E)$  (see Eqns (9) and (22)). In particular, when using the LAX lens mode the separate fits of  $T_{Au}(E)$ ,  $T_{Ag}(E)$  and  $T_{Cu}(E)$  for the respective survey spectra were almost identical. Varying all seven parameters of the model function (see Eqn. (10)) improves the  $\chi^2$  values by  $\sim 20\%$  but results in larger deviations between the individually determined functions  $T_{Au}(E)$ ,  $T_{Ag}(E)$  and  $T_{Cu}(E)$ . Table 4, SSA shows the fitted parameters of the averaged functions  $T_M(E)$  by applying Eqn. (22). Figure 6(a) illustrates the averaged transmission functions. When using the LAX lens mode  $T(E)$  is characterized with the highest increase with decreasing kinetic energies, whereas for SAE 150 mode a smaller increase was obtained.

In order to test the resulting function  $T(E)$  a relative quantification of several lines in a calibration sample was performed. Tables 5(a) (LAE) and 5(b) (LAX and SAE 150) demonstrate the SSA results as well as comparison with the results obtained using Wagner's sensitivity factors ( $SF$ ).<sup>9</sup> The deviation of the quantification obtained according to Eqn. (6) from the true values of 0.333 (using three lines) or 0.5 (using two lines) is in all cases  $<6\%$  (see also Fig. 7(a)). The values resulting from the use of Wagner's sensitivity factors<sup>9</sup> can deviate by up to 30%.

Looking at Table 5(a), column 6, for LAE one can already find quite accurate results for the Au and Ag values. Obviously in the region between 1500 and 700 eV and with  $\Delta E = 50$  eV the functions  $\lambda(E)$  and  $T(E)$  compensate each other ( $\lambda(E) \sim E^{0.6}$  and  $T(E) \sim E^{-0.6}$ ) and the use of  $\sigma$  as sensitivity factor is more preferable than the use of Wagner's sensitivity factors.<sup>9</sup>

For an iterative fit of the  $T(E)$  functions up to 400 000 iteration cycles were applied. On a Pentium-1.6 GHz processor this took a calculation time of  $\sim 15$  min. The advantage of this method is the low expenditure for the measurements, otherwise no reasonable adaptation of the reference spectra to the measured spectra of Au, Ag and Cu could be obtained ( $\chi^{2*} > 200$ , ideal value:  $\chi^{2*} = 1$ )<sup>23</sup> for a small pass energy  $\Delta E = 10$  eV because of high internal electron scattering in the analyser (Fig. 8). This difficulty motivated us to develop the QPA method, building up the transmission function without external reference spectra.

In order to test the **QPA method**, the transmission functions estimated independently by the QPA and SSA methods using  $\Delta E = 50$  eV may be compared. Table 4 shows largely differing parameters for  $T(E)$  from Eqn. (22) but gives almost identical transmission functions (see Fig. 6).

The QPA transmission function calculated for a pass energy of  $\Delta E = 10$  eV is given in Tables 6(a) and 6(b) together with the results of quantification for the lens modes LAE, LAX and SAE 150 using Al/Mg Twin excitation. Figure 7(b) visualizes the deviation of the results calculated according to Eqns (6) and (8) from the true values. For comparison, the results for application of Wagner's sensitivity factors<sup>9</sup> are displayed. The graphs of the corresponding  $T(E)$  functions are shown in Fig. 9.

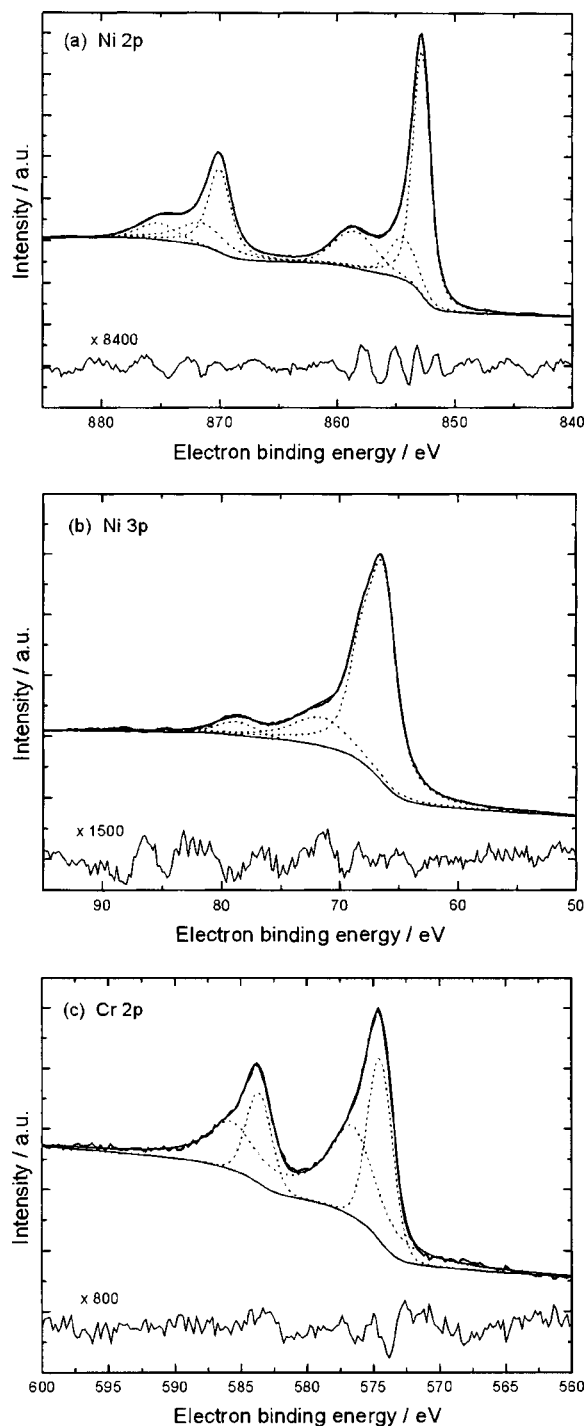
Finally the QPA transmission function was calculated for a monochromatized Al  $K\alpha$  x-ray excitation for  $\Delta E = 10$  and 50 eV and the LAX lens mode. The data obtained are listed in Table 7. Figure 10 compares both transmission functions. The deviation of the results from the expected values in comparison with results using Wagner's sensitivity factors<sup>9</sup> is demonstrated in Fig. 11.

It is clearly visible that the function  $T(E)$  for a 10 eV pass energy has a much steeper increase with falling kinetic energy than the  $T(E)$  functions measured with a pass energy of 50 eV in all lens modes (Figs 6(b), 9 and 10). All parameters calculated using the QPA method are given in Table 8. The deviation of the values obtained with the QPA method from the true values is  $< 7.5\%$  in all cases; the values using Wagner's sensitivity factors<sup>9</sup> deviate by up to 38% (see Tables 6 and 7).

The QPA method can be applied universally for any spectrometers independent of the existence of reference spectra. These advantages exceed the drawback from time-consuming peak-area measurements.

## QUANTITATIVE ANALYSIS OF THE TEST SAMPLE Ni<sub>90</sub>Cr<sub>10</sub>

In order to demonstrate the applicability of the calculated function  $T(E)$ , quantitative analysis of the sample Ni<sub>90</sub>Cr<sub>10</sub>



**Figure 12.** Determination of intensities of Ni 2p (a), Ni 3p (b) and Cr 2p (c) measured at Ni<sub>90</sub>Cr<sub>10</sub> by peak fitting. Solid lines: (top) spectrum; (middle) background; (bottom) residual. Dotted lines: components. Spectrometer setting: Al Twin,  $\Delta E = 50$  eV, LAE.

was performed. This sample is used as a positive pole in K-type thermocouples and comprises 88.3 at.% Ni, 10.5 at.% Cr, 0.16 at.% Fe, 1.04 at.% Si and traces of Co. For the correct relative quantification for NiCr a normalized concentration ratio of 0.894/0.106 is expected (Eqn. (6)). The normalized intensity ratio of  $I_{Ni2p}/I_{Ni3p} \sim 1$  was also tested for this sample.

**Table 9(a).** Comparison of quantification for Ni90Cr10 obtained by SSA transmission functions  $T(E)$  and Wagner's sensitivity factors ( $SF^9$ ) (setting: Al/Mg Twin,  $\Delta E = 50$  eV, LAE)

X-ray source	Line	$E$ (eV)	SSA results <sup>a</sup>						Results after Wagner <sup>a</sup>			
			$\frac{I_{Ai}}{\sum_j I_{Aj}}$	$\sigma_{Ai}(E)$	$\lambda_{Ai}(E)$ (Å)	$T(E_{Ai})$	$\frac{I_{Ai}/[\sigma_{Ai}\lambda_{Ai}T(E_{Ai})]}{\sum_j I_{Aj}/[\sigma_{Aj}\lambda_{Aj}T(E_{Aj})]}$	Error (%)	$SF_{Ai}$	$\frac{I_{Ai}/SF_{Ai}}{\sum_j I_{Aj}/SF_{Aj}}$	Error (%)	
Al $K\alpha$	Ni 3p	1419	0.1251	2.21	20.64	0.850	0.530	+6.0	0.5	0.563	+12.6	
	Ni 2p	626	0.8749	22.1	11.27	1.229	0.470	-6.0	4.5	0.437	-12.6	
Al $K\alpha$	Cr 2p	908	0.3404	11.7	14.74	1.044	0.100	-5.7	2.3	0.101	-4.7	
	Ni 3p	1419	0.6596	2.21	20.64	0.850	0.900	+0.7	0.5	0.899	+0.6	
Al $K\alpha$	Cr 2p	908	0.0687	11.7	14.74	1.044	0.111	+4.7	2.3	0.126	+18.9	
	Ni 2p	626	0.9313	22.1	11.27	1.229	0.889	-0.6	4.5	0.874	-2.2	
Mg $K\alpha$	Ni 3p	1186	0.1289	2.06	18.00	0.925	0.529	+5.8	0.5	0.571	+14.2	
	Ni 2p	392	0.8711	21.2	8.21	1.496	0.471	-5.8	4.5	0.429	-14.2	

<sup>a</sup> The uncertainties of both methods are shown in columns 9 and 12 (see Fig. 13(a), LAE).

**Table 9(b).** Comparison of quantification for Ni90Cr10 obtained by SSA transmission functions  $T(E)$  and Wagner's sensitivity factors  $SF^9$  (setting: Al/Mg Twin,  $\Delta E = 50$  eV, LAX and SAE 150; see also Fig. 13(a), LAX and SAE 150)

X-ray source	Line	$E$ (eV)	LAX				SAE 150			
			SSA results		Results after Wagner		SSA results		Results after Wagner	
			Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Al $K\alpha$	Ni 3p	1419	0.504	+0.8	0.527	+5.4	0.501	+0.2	0.588	+17.6
	Ni 2p	626	0.496	-0.8	0.473	-5.4	0.499	-0.2	0.412	-17.6
Al $K\alpha$	Cr 2p	908	0.104	-1.9	0.106	0	0.110	+3.8	0.099	-6.6
	Ni 3p	1419	0.896	+0.2	0.894	0	0.890	-0.5	0.901	+0.6
Al $K\alpha$	Cr 2p	908	0.105	-0.9	0.117	+10.4	0.110	+3.8	0.136	+28.3
	Ni 2p	626	0.895	+0.1	0.883	-1.2	0.890	-0.5	0.864	-3.4
Mg $K\alpha$	Ni 3p	1186	0.529	+5.8	0.541	+8.2	0.506	+1.2	0.611	+22.2
	Ni 2p	393	0.471	-5.8	0.459	-8.2	0.494	-1.2	0.389	-22.2

**Table 9(c).** Comparison of quantification for Ni90Cr10 obtained by QPA transmission functions  $T(E)$  and Wagner's sensitivity factors  $SF^9$  (setting: Al/Mg Twin,  $\Delta E = 10$  eV, LAE, LAX and SAE 150; see also Fig. 13(b))

X-ray source	Line	$E$ (eV)	LAE				LAX				SAE 150			
			QPA results		Results after Wagner		QPA results		Results after Wagner		QPA results		Results after Wagner	
			Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Al $K\alpha$	Ni 3p	1419	0.502	+0.4	0.416	-16.8	0.497	-0.6	0.395	-21.0	0.505	+1.0	0.543	+8.6
	Ni 2p	626	0.498	-0.4	0.584	+16.8	0.503	+0.6	0.605	+21.0	0.495	-1.0	0.457	-8.6
Al $K\alpha$	Cr 2p	908	0.099	-6.6	0.126	+18.9	0.111	+4.7	0.139	+31.2	0.103	-1.9	0.102	-2.8
	Ni 3p	1419	0.901	+0.8	0.874	-2.3	0.889	-0.6	0.861	-3.7	0.897	+0.4	0.898	+0.5
Al $K\alpha$	Cr 2p	908	0.100	-5.7	0.093	-12.3	0.099	-6.6	0.112	+5.7	0.105	-1.0	0.119	+12.3
	Ni 2p	626	0.900	+0.7	0.907	+1.5	0.901	+0.8	0.888	-0.7	0.895	+0.1	0.881	-1.4
Mg $K\alpha$	Ni 3p	1186	0.513	+2.6	0.393	-21.4	0.538	+7.6	0.425	-15.0	0.540	+8.0	0.589	+17.8
	Ni 2p	393	0.487	-2.6	0.607	+21.4	0.462	-7.6	0.575	+15.0	0.460	-8.0	0.411	-17.8

Measurements were made with a mechanically polished Ni90Cr10 foil sputtered with 5 keV argon ions for at least 30 min until the concentrations of oxygen and carbon were <6 at.%. Spectra were recorded using

Al/Mg Twin and Al Mono excitation,  $\Delta E = 10$  and 50 eV and lens modes LAE, LAX and SAE 150. These conditions agree with those of the reference spectra records.

**Table 9(d).** Comparison of quantification for Ni90Cr10 obtained by QPA transmission functions  $T(E)$  and Wagner's sensitivity factors  $SF^9$  (setting: Al Mono,  $\Delta E = 10$  and 50 eV, LAX; see also Fig. 13(c))

Line $A_i$	$E$ (eV)	$\Delta E = 50$ eV				$\Delta E = 10$ eV			
		QPA results		Results after Wagner		QPA results		Results after Wagner	
		Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
Ni 3p	1419	0.497	-0.6	0.549	+9.8	0.504	+0.8	0.432	-13.4
Ni 2p	626	0.503	+0.6	0.451	-9.8	0.496	-0.8	0.568	+13.4
Cr 2p	908	0.108	+1.9	0.106	0	0.102	-3.8	0.136	+28.3
Ni 3p	1419	0.892	-0.3	0.894	0	0.898	+0.5	0.964	-7.8
Cr 2p	908	0.101	-4.7	0.126	+18.9	0.111	+4.7	0.106	0
Ni 2p	626	0.899	+0.6	0.874	-2.3	0.889	-0.6	0.894	0

The peak areas were determined by peak-fit-adapting the experimental Ni 2p (Fig. 12(a)) and Ni 3p (Fig. 12(b)) signals using three doublets and the signal of Cr 2p using two doublets (Fig. 12(c)). The excitation satellites were subtracted and background correction (Eqn. (21)) was integrated into the peak-fitting process. Background determination by subtracting a Shirley background (start calculation and one iteration) has given very similar results.

The  $\lambda$  values of Ni and Cr for Ni90Cr10 were calculated using the TPP-2M formula<sup>18</sup> for inorganic compounds, with stoichiometry coefficients of 0.894 and 0.106 for Ni and Cr, respectively,  $N_V^{NiCr} = 9.576$  ( $N_V^{Ni} = 10$ ,  $N_V^{Cr} = 6$ ) and  $\rho_{Ni90Cr10} = 8.5$  g cm<sup>-3</sup>. Tables 9(a) and 9(b) show the SSA results and Tables 9(c) and 9(d) show the QPA results in comparison with those obtained by using Wagner's sensitivity factors.<sup>9</sup> Figure 13 illustrates the deviation compared with the true values according to Eqns (6) and (8) for Ni/Cr and Ni 3p/Ni 2p. In the case of Mg Twin excitation, the Cr 2p signal could not be analysed because of the strong Ni LMM signal.

The results determined using Eqns (6) and (7) show very good agreement with the nominal values in all experimental settings. For every analysis the error was <8%, although the intensity ratio of the evaluated spectra differed strongly for each spectrometer setting. In 3 of 24 cases the use of Wagner's sensitivity factors<sup>9</sup> gave good results (Fig. 13(a) LAX, B; Fig. 13(c)  $\Delta E = 50$  eV, B; Fig. 13(c)  $\Delta E = 10$  eV, C), contrasting with deviations of >30% in the other 21 cases.

## OPERATING THE PROGRAM

Using the new routine in UNIFIT 2004,<sup>24</sup> a user has two different ways to determine the transmission function of the spectrometer. Both the SSA and QPA methods allow optional adaptation of the model function (Eqn. (10)), either fixing or adjusting individually seven parameters. The resulting  $T(E)$  functions can be stored, shown and used for quantification. Figure 14 shows the dialogue with the necessary data. For a first proposal,  $\lambda$  is calculated from

the approximation

$$\bar{\lambda} = \bar{k} \cdot E^{\bar{m}} \quad (24)$$

with  $\bar{k} = 0.103$  and  $\bar{m} = 0.745$  (mean values calculated from table 1 of Tanuma *et al.*,<sup>25</sup> valid over an energy range 500–2000 eV). The user, if desired, may edit the fields 'Sigma', 'Lambda' and 'IERF'.

## The SSA method

After importing a measured survey spectrum of Au, Ag or Cu, the relevant reference spectra will be loaded and shown as well. A dialogue for the input of the start parameters for adaptation of the reference spectra to the measured spectra by varying the free parameters opens automatically (Fig. 15). Optionally, the function  $T(E)$  may be normalized ( $T(1000 \text{ eV}) = 1$ ). Then, the number of iterations has to be selected ('Number of iterations' multiplied by 'Number of cycles'). Even an amount of >200 000 iterations may be reasonable. The iteration process can be observed and aborted any time, to be restarted with new improved parameters.

After determining the functions  $T_{Au}$ ,  $T_{Ag}$  and  $T_{Cu}$  for Au, Ag and Cu, the arithmetic mean value  $T_M$  of the functions (see Eqn. (12)) may be calculated in subroutine 'Modify—Spectrum Operation', and the parameters of  $T_M$  are verified by an additional fit.

## The QPA method

In the QPA method the reference ratios (see Eqn. (16)) for nine standard peaks 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 3d and Ge 2p<sub>3/2</sub> are utilized for the determination of  $T(E)$ . The program routine 'Concentration' of UNIFIT 2004 may be used for this operation. For calculation of the reference ratio  $r_{A_i}$  the user have to set the  $T(E)$  (IERF) always to unity. It is essential that the sum of the reference ratios of each standard sample amounts to 100%. Following the input of the data in the respective dialogues, the model function (Eqn. (10)) may be selected (Fig. 16). Depending on the number of free parameters, a calculation time of between a few seconds (for three parameters) and 15 min (for seven parameters) is necessary when a Pentium III-1.6 GHz processor is used.



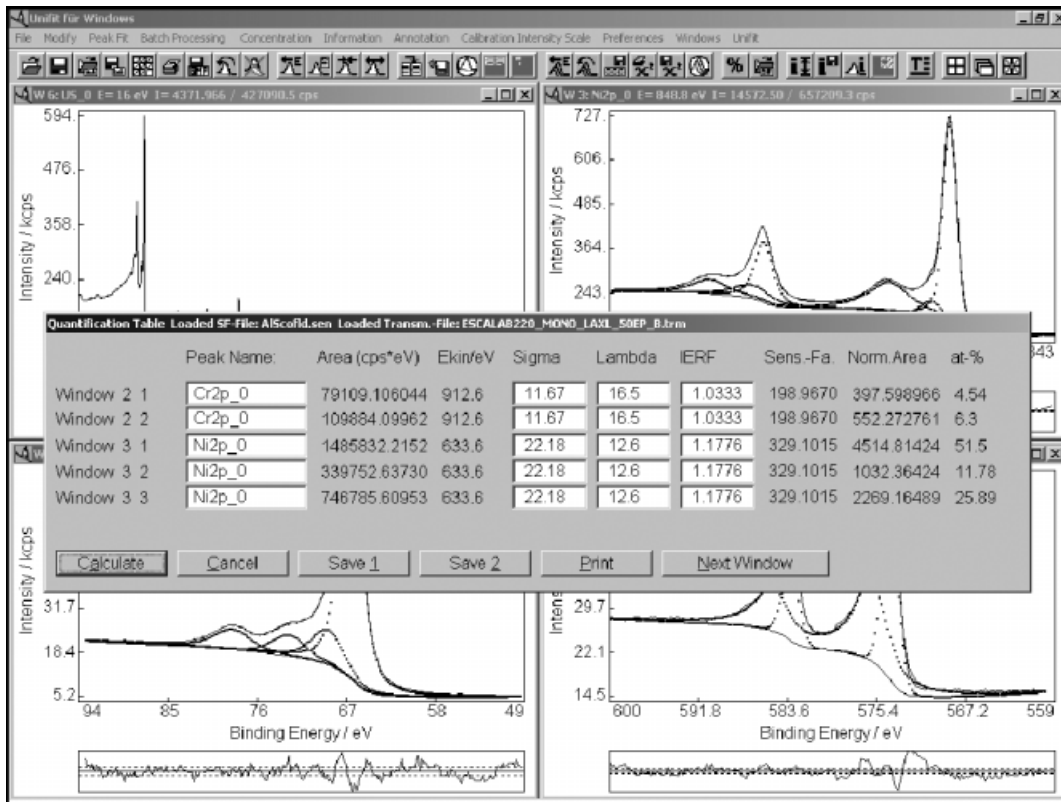


Figure 14. Dialogue of the quantification using the sensitivity factor defined by the product of  $\sigma$ ,  $\lambda$  and the particular transmission function  $T(E)$  (IERF) integrated in software UNIFIT 2004.<sup>24</sup>

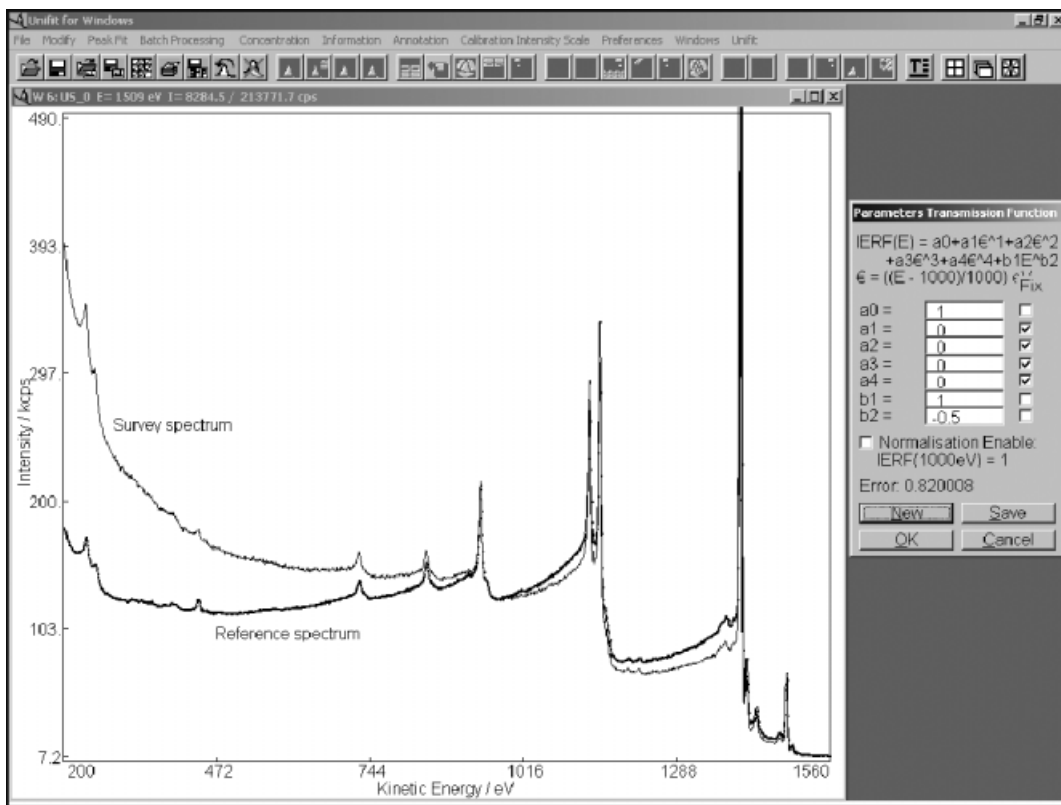
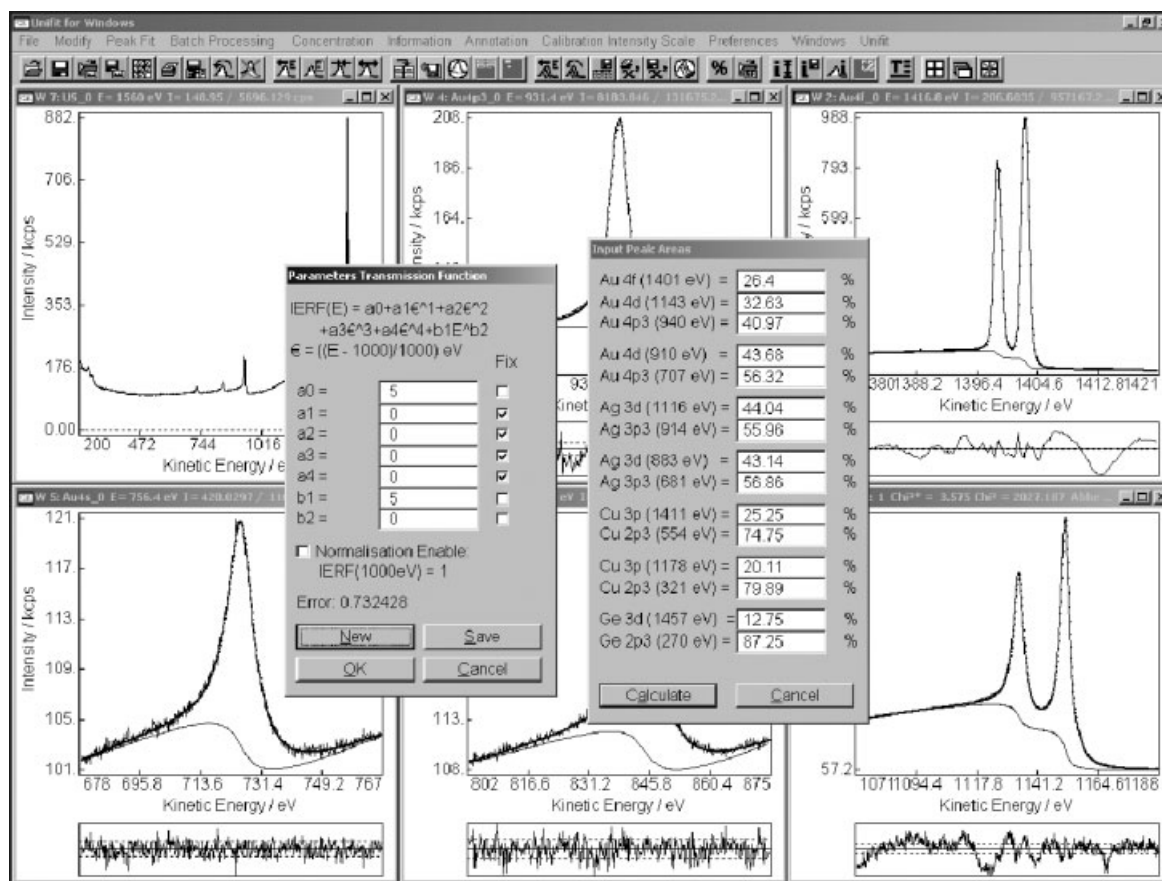


Figure 15. Dialogue to create the model function for estimating  $T(E)$  (IERF) by means of the SSA method integrated in UNIFIT 2004.<sup>24</sup>



**Figure 16.** (Left window) Dialogue to create the model function for estimating the transmission function  $T(E)$  (IERF) via QPA. (Right window) Input dialogue for the normalized intensities of standard peaks Au, Ag, Cu and Ge.

## SUMMARY

It is shown that the accuracy of the quantification obtained from XPS peak intensities can be improved significantly by using predetermined transmission functions  $T(E)$ . Two different calibration methods for estimating  $T(E)$  are presented: a survey spectra approach (SSA) and a quantified peak-area approach (QPA) for minimizing the quantification error. Both methods can be applied for determining the transmission function  $T(E) = a_0 + b_1E^{b_2}$ , alternatively giving comparable results for spectra recorded using Al/Mg Twin excitation and a pass energy of  $\Delta E = 50$  eV. A higher internal scattering of photoelectrons in the analyser when measuring with  $\Delta E = 10$  eV prevents satisfactory adaptation of the reference survey spectra by SSA. The transmission function can be estimated successfully in such a case by means of the new QPA method.

Measurements of the test alloy Ni90Cr10 demonstrated that the SSA and QPA functions,  $T(E)$ , give excellent results also for normalized intensities of Ni 2p and Ni 3p signals. In all studied cases the deviations of the obtained quantification from the true values were <8%, whereas the values resulting from the use of Wagner's sensitivity factors may deviate by up to 38%.

We recommend the following procedure for quantitative analysis with XPS:

- (1) Determination of the function  $T(E)$  of the spectrometer setting used.
- (2) Employment of the  $\sigma$  values of Scofield<sup>20</sup> or Band *et al.*<sup>21</sup> (except the values for the 4f lines).
- (3) Employment of the recommended  $\lambda$  values from the NIST database.<sup>18</sup>
- (4) Consistent determination of the areas of all relevant peaks by means of peakfitting with an adjustable background or an individual background correction.
- (5) Quantification using the relative intensities of the applied spectra and the sensitivity factor  $\sigma \cdot \lambda(E) \cdot T(E)$ .

Only small deviations between results for the reference and the test samples using different parameters of the Escalab 220 iXL spectrometer setting indicate the reliability of the SSA and QPA methods.

New routines for the determination and application of the transmission function for individual spectrometers and their variable settings were embedded into the software UNIFIT 2004, making quantitative analysis from XPS data easier.

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