CONSIDERATIONS ON THE DETECTION LIMIT OF TEY (TOTAL ELECTRON YIELD)

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ABSTRACT
The present state of TEY allows in the medium and high Z-range of elements for values of detection limits between the two established methods XFA and XPS (x-ray photoelectron spectrometry). Thus, in standard geometry we obtained for Cr (K-edge jump) detectable layer thicknesses of 0.2nm. An essential improvement is obtained by a variation of the angle of incident x-rays towards grazing incidence, an increase of the solid angle of electron acceptance and an increase of the monochromatic photon flux by the use of a focusing monochromator. This can improve the detection limit of TEY by two orders of magnitude and it becomes comparable to XPS.

DETECTION LIMIT OF TEY
An irradiation of thin solid films by x-rays gives rise to an emission of photo-, Compton-, Auger- and secondary electrons. In general these electrons lose energy by inelastic collisions during their path from the point of origin to the surface. The detection of the total electron yield is performed without energy dispersion. We observe a jumplike increase of the total electron yield as the irradiation is performed with monochromatic x-radiation in combination with a systematic variation of the photon energy from a few 100eV below an absorption edge of the investigated specimen to a few 100eV above the absorption edge. Besides numerous other parameters the amplitude of the jump depends on the film thickness. Fig.1 depicts the...
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measured Cr K-TEY responses from 5.75keV to photon energies of 5.95keV where the electron yield starts to depart into the edge region by a linear least squares fit. The number of data points for the lsf-calculation is 21. The intersection of this line with the vertical line at 5.989keV defines the lower point of the TEY-jump. Similarly, the upper point of the TEY-jump is found from the intersection of the linear least squares fit through 21 measured data points from 6.02keV to 6.22keV with the vertical line at 5.989keV. The usual definition of the detection limit asks for a characteristic signal of three times the standard deviation of the background. Thus, we adopt the meaning of our measured quantities to this definition.

For quantification of the background we deal with the linear lsf in the lower energy range. The abscissa \( x_i \) is measured with regard to the absorption edge at energy \( E_{Cr\ K-edge} \) and is given by \( x_i = E_i - E_{Cr\ K-edge} \). As the statistical weight of the complete set of the 21 data points is assumed to be identical the error definition of the linear lsf becomes

\[
\nu_i = y_i - a - b \cdot x_i
\]

with the intersection \( a \) at \( x=0 \) and the slope \( b \) of the linear fit. The chi-square merit function is

\[
\chi^2(a, b) = \sum_{i=1}^{N} \nu_i^2
\]

and from the minimum conditions of the chi-square merit function

\[
\frac{\partial \chi^2(a, b)}{\partial a} = 0 \quad \text{and} \quad \frac{\partial \chi^2(a, b)}{\partial b} = 0
\]

follow

\[
a = \frac{S_x \cdot S_y - S_x \cdot S_{xy}}{N \cdot S_{xx} - S_x^2} \quad \text{and} \quad b = \frac{N \cdot S_{xy} - S_x \cdot S_y}{N \cdot S_{xx} - S_x^2}
\]

with the abbreviations

\[
S_x = \sum_{i=1}^{N} x_i, \quad S_y = \sum_{i=1}^{N} y_i, \quad S_{xy} = \sum_{i=1}^{N} x_i \cdot y_i, \quad S_{xx} = \sum_{i=1}^{N} x_i^2
\]

\( N \) is the number of data points (21). The standard deviation \( \sigma(y_i) \) of the data points from the linear fit is

\[
\sigma(y_i) = \frac{1}{N-1} \sum_{i=1}^{N} (y_i - a - b \cdot x_i)^2
\]

and the standard deviation \( \sigma_a \) of the intersection at \( a \) is obtained from \( \sigma(y_i) \) by

\[
\sigma_a = \sigma(y_i) \cdot \sqrt{\frac{S_{xx}}{N \cdot S_{xx} - S_x^2}}
\]

\( \sigma_a \) is equal to the interesting standard deviation \( \sigma_{background} \). Our evaluation routine computes the linear fit, the ordinate \( a \) of the intersection, the \( \sigma_a \)-value and the jump. The definition of the detection limit asks for the characteristic signal. This characteristic signal is given by \( 3\sigma_a \). The meanvalue of the standard deviations of Table 1 is \( \sigma_a = 0.28 \) electrons/10⁴ photons and thus, the characteristic signal is \( 3 \cdot 0.28 = 0.83 \) electrons/10⁴ photons. As the dependence of the Cr K-jump versus filmthickness is computed an initial slope of \( 3.7 \) electrons/(10⁴ photons · nm) is found and the corresponding minimum detectable filmthickness (detection limit) of thin films of Cr becomes \( 0.83/3.7 = 0.23 \)nm. This is less than 1 monolayer of Cr. The uncertainty of the lower and of the upper jump points is governed by

i. structures of the absorption behaviour of the specimen,
ii. irregularities of the spectral distribution of the x-ray source and
iii. countrate statistics.
deviation $\sigma(y_i)$ at energy position $x_i$ is directly proportional to the square root of the number $y_i$ of detected electrons (count rate times data acquisition time) and the relative error $\varepsilon_i$ is

$$\varepsilon_i = \frac{\sigma(y_i)}{y_i} = \frac{1}{\sqrt{y_i}}$$

<table>
<thead>
<tr>
<th>film thickness (nm)</th>
<th>$\sigma_a$ (electrons/10⁴ photons)</th>
<th>Cr K-jump (electrons/10⁴ photons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.28</td>
<td>23.8</td>
</tr>
<tr>
<td>20</td>
<td>0.31</td>
<td>36.6</td>
</tr>
<tr>
<td>40</td>
<td>0.20</td>
<td>55.1</td>
</tr>
<tr>
<td>60</td>
<td>0.28</td>
<td>67.1</td>
</tr>
</tbody>
</table>

Table 1 Numerical evaluations of the measured responses of Fig.1

The relative error of the lower jump point depends on the number $N$ of data points and on the relative errors $\varepsilon_i$ of the individual data points. It can be assumed that $\sigma_f / a$ is directly proportional to the averaged relative errors $\varepsilon_i$. Thus, an increase of the flux of monochromatic primary x-ray photons and of detected electrons increases the measured value from $y_i$ to $k \cdot y_i$ and decreases the relative error from $\varepsilon_i$ to $\varepsilon_i / \sqrt{k}$ and the relative standard deviation from $\sigma_f / a$ to $\left( \sigma_f / a \right) / \sqrt{k}$. With $k = 10^4$ the value of the intersection becomes $10^4 \cdot a$, the characteristic jump from the layer under investigation increases towards $10^4$ times of its original value and the detection limit is improved to $1/ \sqrt{10^4} = 10^{-2}$ of its former value. An increase of $y_i$ can be performed by greater x-ray photon fluxes, detection of the total amount of electrons leaving the specimen surface and an increase of the data acquisition time. In its present configuration our experimental setup provides minimum data acquisition times of the Cr K-TEY responses of Fig.1 of one and even more hours. The goal of the following considerations should be a reduction of the data acquisition time in combination with an improved detection limit.

Greater x-ray photon fluxes are obtained by

i. a higher specific flux density of photons $s^{-1}sr^{-1}mA^{-1}keV^{-1}$ from the x-ray tube,
ii. monochromator crystals with improved reflection properties and
iii. an increase of the solid angle of accepted tube radiation.

The first possibility can be realized by a proper choice of the x-ray tube target material in combination with an optimum pair of tube voltage and tube current. The third possibility is realized by a change from a plane crystal monochromator to a focusing arrangement.

The magnitude of the detected electron flux can be increased by

iv. a variation of the x-ray incidence angle with regard to the specimen surface,
v. a variation of the solid angle of electron detection and
vi. a variation of the detector bias.

At constant beam divergence a reduction of the incidence angle towards grazing incidence and total reflection causes an enlargement of the irradiated specimen area and an absorption of incident x-rays closer to the specimen surface. Electrons expelled near by the surface have an increased escape probability. In our present experimental setup the cone angle is $+20^\circ$ and the detection of low energy secondary electrons is suppressed by a bias of $-40$V.
acceptance should be chosen close to $2\pi$ and an essential increase of the number of detected electrons can be realized by a removal of the grid.

**X-RAY PHOTON FLUX**

The TEY-responses of Fig.1 have been measured with a rotating Cu-anode, a take-off angle of x-rays from the target of 6°, a flat Ge (111) monochromator crystal and a solid angle of x-ray acceptance of $6.25 \cdot 10^{-6}$ sr.

A first possibility for an essential improvement of the photon flux from the tube target seems to be a proper choice of the target material. Therefore, we computed the spectral responses of continuous radiation\(^3\) for Cu, Ag and W (Fig.2). In the photon energy interval close to the Cr K-edge the flux from the Cu-target is greater when compared to Ag or W. At photon energies greater than the energies corresponding to the W L-edges the specific flux from the W-target reaches the expected value of approximately twice the flux from the Cu-target. A decision on the best target material can be made only after comparison of the spectral responses.

![Computed x-ray tube spectra for different target materials (take-off angle 6°)](image)

**Fig.2** Computed x-ray tube spectra for different target materials (take-off angle 6°)

Another essential parameter is the choice of tube voltage and tube current for a given target material and constant tube power. Fig.3 depicts computed responses for Cu target, take-off angle of 6° and a constant power of 30W. Tube voltages have been varied from 10 to 40kV. As can be seen the combination 20kV/1.5mA delivers the highest flux in the Cr K-edge region.
Fig. 3 Computed x-ray tube spectra from a tube with Cu-target for different acceleration voltages at constant power of 30W (take-off angle 6°)

Fig. 4 Measured x-ray tube spectrum. Cu-anode 30kV/100mA, entrance slit H=2mm, W=0.1mm, exit slit H=3mm, W=0.1mm. Ge(111) monochromator

Fig. 5 Measured x-ray tube spectrum. Cu-anode 30kV/100mA, entrance slit H=2mm, W=0.1mm, exit slit H=3mm, W=0.1mm. Si(111) monochromator
For our instrument we use either a flat Si (111)- or a flat Ge (111)-crystal. Figs. 4 and 5 compare the photon fluxes from a Cu tube operated at 30kV/100mA, take-off angle of 6° and measured with either Ge(111) or Si(111) and identical settings of the spectrometer slits. Up to 20keV the Ge-crystal dominates. The behaviour inverts for higher photon energies in favour of the Si-crystal. In case of an investigation of Cr the Ge-crystal gives three times the monochromatic flux of the Si-crystal. The decision on the monochromator crystal asks for a comparison of measured spectral responses.

Fig. 6 Johansson monochromator r=140mm, x=90mm, θ=18.75°

Fig. 7 Johansson monochromator r=140mm, x=180mm, θ=40.01°
The solid angle of x-ray acceptance of the monochromator system with regard to the point source on the x-ray tube target of our instrument is given by the dimensions of the exit slit system in TEY-work. Typical values are height 3mm and width 0.5mm. With an effective distance from the point source of 490mm follows a solid angle of $6.25 \times 10^{-6}$sr. A change to a focusing monochromator with curved crystal gives an increase of the solid angle of x-ray acceptance. Figs.6 and 7 depict the geometry of a wavelength dispersive monochromator system used in EPMA. $x$ is the distance between source and crystal, $\theta$ the Bragg angle and $r$ the radius of the Rowland circle. Two different diffraction angles are shown in order to illustrate that the horizontal beam divergence in the plane of Figs.6 and 7 remains unchanged. A typical length of the crystal is 24mm, the radius of the Rowland circle is 140mm and the accepted horizontal beam divergence becomes $\alpha=24/(2 \cdot 140)$rad. Under the assumption that the vertical divergence is identical with our present configuration, it follows that $\beta=3/490$rad and the solid angle of x-ray acceptance of the focusing system becomes $5.25 \times 10^{-4}$sr. Thus, a gain of nearly two orders of magnitude (84 times) comes from the replacement of the flat crystal by a focusing arrangement.

**DETECTED ELECTRON FLUX**

It becomes possible to detect low energy secondary electrons as the bias of the channeltron detector is changed from -40V to 0V and consequently, the amount of detected electrons increases by a factor 6. The explanation for the rejection of secondary electrons by means of a bias can be given by the mechanisms for the creation of photo-, Auger- and secondary electrons. Whereas in case of photo- and Auger-electrons after their formation as a consequence of photoelectric absorption only elastic and inelastic collisions have to be considered, secondary electrons ask for an additional consideration of their formation by electrons of different kinetic energies. Thus, the algorithms for numerical evaluations of measured TEY-results become more complicated. In an earlier paper we have shown that in quantitative surface analysis the use of normalized TEY-jumps from measurements performed with and without bias and different analytical results. Concentrations which have been

![Fig.8 Computed Cr K-TEY signals in dependence on the cone angle. The cone angle is measured from the cone axis. The parameter of the curves is the incidence angle of x-rays.](image-url)
agreement with the expected values and the differences to the concentrations from measurements without bias are a few weight percent. Thus, from investigations of thin films by TEY we expect no essential differences between the normalized film thickness dependences of TEY-jumps from measurements performed with and without bias.

Another possibility for an increase of the detected electron flux comes from the incidence angle of monochromatic x-ray photons with regard to the specimen surface and from the solid angle of electron detection. In our instrument we use an incidence angle of 12° and a cone of detection of ±20°. Fig. 8 shows the dependence of the TEY-signal on the cone angle with the incidence angle as parameter. Our geometry is given by the data point on the 12°-curve at the cone angle 20°. The numerical value of the TEY-signal is 0.00787. By changing the geometry to 6° and an acceptance cone of 80° we obtain a gain of 8 of the TEY-signal.

CONCLUSIONS
A combination of the possibilities to increase the flux of monochromatic x-rays should give a gain of the TEY-signal of at least 100 and from the possibilities to increase the detected electron flux a further gain of at least 50 has to be expected. A total gain of 10⁴ becomes possible as the width of the energy window of the monochromator is made twice its present value. Thus, an improvement of the Cr detection limit of TEY from 0.2 nm to 2 pm can be realized by a systematic change of the experimental setup.

REFERENCES
3 Ebel, H., X-Ray Spectrom. (in press)