QUANTITATIVE ANALYSIS BY X-RAY INDUCED TOTAL ELECTRON YIELD (TEY) COMPARED TO XRFA

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ABSTRACT

The theoretical concepts of the two methods are similar. Consequently, comparable fundamental parameter algorithms can be developed and applied to quantitative analysis of bulk specimens and to investigation of thin layers by TEY and by XRFA. Whereas the sampling depth of XRFA is determined by photoelectric absorption, for TEY the escape probability of electrons reduces this quantity to values of less than 100 nm. Thus, TEY is practically a surface analytical method with sampling depths between x-ray photoelectron spectrometry and XRFA. The decrease of fluorescence yields with decreasing atomic number Z is responsible for a significant reduction of the elemental sensitivity of XRFA in the range of low Z elements. On the other hand, the elemental sensitivity of TEY increases with decreasing Z as a consequence of the dominating contribution of KLL- and LMM-Auger electrons to measured TEY jumps. The possibility to quantify submonolayers and layers of nm-thickness buried under nm-layers, a nearly linear dependence of TEY signals versus elemental concentration of multielement specimens and the EXAFS and XANES information which is contained in measured TEY responses are valuable features of TEY. A disadvantage of TEY is the time consuming sequential data accumulation of TEY spectra when compared to energy dispersive XRFA. But due to progress in instrumentation TEY is no longer reserved to synchrotron radiation sources.

ABSORPTION-EDGE JUMPS OF TEY

TEY deals with the quantification of x-ray induced electron emission. Measurements are performed with tunable monochromatic x-ray sources and nondispersive electron detection.

Fig.1 Measured Cr-K-TEY signal versus photon energy from Cr layer with thickness of 500 nm on Fe substrate. The distance between the intersections (black squares) of the linear least squares fits through the measured responses below and above the Cr-K edge with the vertical line at the Cr-K-edge position (5.989 keV) defines the jump.
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The information on compositions and layer thicknesses is obtained from the jumplike increase of the electron emission when tuning the photon energy from below to above the absorption-edge energies of the chemical elements under consideration. Fig.1 shows a measured response of the x-ray induced electron signal of Cr in the vicinity of the Cr-K edge. For the measurements the setup of Fig.2 was employed. The Cr-K jump of Fig.1 appears at photon energy of 5.989 keV. For quantification of the jump the measured responses from 5.75 up to 5.95 keV and from 6.05 up to 6.25 keV are described by the dotted linear responses which are obtained from least squares fits to the measured TEY signals. The intersections of the lines with the vertical line at edge position are characterized by full squares and the distance between the two squares gives the numerical value of the jump. Consequently, a jump of 80 follows from Fig.1.

A spectral width of more than 50 eV of the tunable monochromator helps to reduce the contributions of XANES signals to the measured TEY responses and consequently to the result of jump evaluations. The halfwidth of 40 eV at photon energy of 10 keV of the setup of Fig.2 is responsible for the occurrence of weak XANES signals in the TEY response at photon energies above the Cr-K edge of Fig.1. The influences of statistical errors, spectral width of the monochromatic x-ray beam and the energy range of linear least squares fits on the significance and detection limits of TEY were treated in earlier investigations 1-8.

**Fig.2** Experimental setup for TEY measurements with x-ray tube (rotating anode system), tunable flat crystal monochromator and electron detection by channeltron.

**Fig.3** TEY response of Cu measured by the setup of Figs.4 with Fe standard diffraction tube, operated at 30 kV, 30 mA. XANES and EXAFS structures appear at photon energies above the Cu-K edge at 8.979 keV.
A second essential source of information of TEY are the XANES signals. Fig.3 gives the TEY response of Cu with well resolved oscillations from XANES as measured by the setup given by Fig.4. The result of Fig.3 is an evidence for the comparably higher spectral resolution of an instrument with tunable focussing monochromator. Spectral halfwidths of 15 eV or better at photon energies of 10 keV are required for a reliable reproduction of the XANES responses. Details on the evaluation and interpretation of XANES signals can be gained from literature.

Fig.4 Experimental setup for TEY measurements with x-ray tube (standard x-ray diffraction tube), tunable curved crystal monochromator (Johann geometry) and measurement of the current of emitted electrons by pA-meter.

The analytical information of XRFA on composition and layer thicknesses comes from the characteristic lines of the elements. The corresponding quantity of TEY are the absorption-edge jumps. The XANES signals of TEY are an additional source of structural information on the matrix where the atoms are embedded.

Whereas the characteristic lines of XRFA can be measured simultaneously by an energy dispersive detection system, TEY suffers from the sequential accumulation of data. The jumps are measured stepwise with step widths of a few eV over an energy range of approximately 500 eV. This time consuming procedure asks for one hour and even more per jump and explains why up to now TEY is primarily applied to XANES and EXAFS studies and most of the experiments are performed with synchrotron radiation sources.

But there exists a second important feature of TEY. The sampling depth of TEY is roughly three orders of magnitude smaller when compared to XRFA. From this point of view TEY is a surface analytical tool similar to Auger electron and x-ray photoelectron spectrometry.

INSTRUMENTATION

Instruments with sufficient photon fluxes are necessary to develop TEY towards an x-ray analytical tool for quantitative surface analysis. As synchrotron radiation sources are excluded there remain systems with rotating anode sources and tunable focussing monochromators.

TEY measurements are performed either under vacuum, ambient atmosphere or under reduced gas pressure. Figs.2 and 4 illustrate two different setups for TEY. The setup of Fig.2 with nonfocussing monochromatization by flat crystal, a rotating anode source and electron detection by channeltron is operated under vacuum conditions. The rate of detected electrons depends on the flux of monochromatic x-ray photons and on the electron yield. Yields of 0.001 to 0.01 electrons per photon are realistic values. Rates of $10^2$ to $10^4$ electrons
per second can be expected. Another essential quantity of an instrument with flat crystal is a spectral resolution of approximately 40 eV for photon energies of 10 keV. An essential advantage of this kind of TEY instrument is the possibility to perform experiments under variable incidence angles of x-rays and take-off angles of electrons.

The setup of Fig.4 with focussing monochromator, a standard diffraction tube as x-ray source and gas amplification in ambient atmosphere gives currents up to 1 pA. A spectral resolution of less than 15 eV for photon energies of 10 keV characterizes this kind of instrumentation. It becomes evident from the foregoing considerations that the setup of Fig.2 fullfills only the requirements for an application to analytical TEY, whereas the setup of Fig.4 can be used for both, analytical TEY and XANES.

Fig.5 TEY instrument based on the principle of Fig.4 with x-ray tube, focussing monochromator in Johann geometry and specimen stage.

A combination of rotating anode source and focussing monochromator is the most perfect solution for a laboratory TEY equipment. It has to be mentioned that the minimum distance between tube target and the monochromator crystal is responsible for the upper limitation of the photon energy range and the minimum distance between specimen stage and target restricts the maximum photon energy. As a consequence of these two details careful considerations on the energy range, the radius of the Rowland circle, selection of monochromator crystals, a decision on operation under vacuum or under ambient atmosphere and definition of the most efficient rotating anode system are necessary.
There remains one disadvantage of tube systems. This is the occurrence of higher order monochromatic radiation. The much higher photon flux of synchrotron radiation sources allows to suppress diffraction of harmonics by installation of double crystal monochromators.

**QUANTITATIVE ANALYSIS BY TEY**

![Graph showing Ga-K jumps from measured jumps (exp) and computed values (theor).](image)

**Fig.6** Relative Ga-K jumps from measured jumps (exp) and computed values (theor). Computations were performed under the assumption of composition and thickness values of the specimens given by the supplier.

The determination of compositions by TEY is demonstrated on the example of the ternary system Al$_x$Ga$_{1-x}$As. Fig.6 gives Ga-K jumps of pure GaAs and of eight thin layers with variable Al content $x$ and different layer thicknesses. For comparison with theoretical data relative jumps are used. This is the jump expressed in units of the Ga-K jump of pure GaAs. The magnitude of the jumps depends on the composition and on the layer thickness. An increasing Al content $x$ causes due to the dominating role of the composition at layer thicknesses of more than 50 nm a decreasing Ga-K jump. Fig.6 provides experimental relative jumps (crosses) and theoretical values (squares) in dependence on the Al concentration. For computations the thicknesses and compositions as given by the supplier of the Al$_x$Ga$_{1-x}$As layers were used. Further investigations on quantitative TEY were performed on the binary alloy systems Au-Cu and Au-Pd and a basic contribution to quantitative TEY was made by Ghassemi.

Another application of TEY are thickness determinations of thin layers. The principle of thickness determinations by information from layer signals is shown on the example of thin Cr layers on Fe substrates. Cr-K jumps were measured in the range of photon energies from 5.65 to 6.30 keV. In case of thin Cr layers normalized jumps are given in units of the K jump of bulk Cr. Fig.7 compares computed and measured normalized Cr-K jumps in dependence on the layer thickness. The second example is the thickness determination by information from substrate signals. This is treated by thin Cr layers on Ti substrates. Ti-K jumps were measured in the range of photon energies from 4.7 to 5.2 keV. Normalized jumps are given in units of the K jump of bulk Ti without Cr layer. Fig.8 compares computed and measured normalized Ti-K jumps in dependence on the layer thickness.
The results of both thin layer experiments give an impression on the sampling depth of TEY. Under the assumption of an exponential dependence between signal and thickness follows a sampling depth of less than 100 nm. A more detailed treatment of possible emissions of electrons and characteristic radiations after photoelectric absorption in the K shell indicates the occurrence of a variety of Auger electrons from nonradiative transitions and of photoelectrons from photoelectric absorption of characteristic radiations after radiative transitions \(^{1,13,15,16,21}\).

**Fig. 7** Comparison of the theoretical response of normalized Cr-K jumps versus thickness of the Cr layer and results of our experiments. TEY jumps of thin Cr layers on Fe substrates were measured by the experimental setup of Fig. 2 with rotating Cu anode, 30 kV, 100 mA and Ge(111) crystal. Thicknesses of the layers were chosen from 10 to 500 nm.

**Fig. 8** Normalized Ti-K jumps of Ti substrates covered with thin Cr layers (data points are from experiments) and theoretical response (curve). TEY responses of thin Cr layers on Ti substrates were measured by the experimental setup of Fig. 2 with rotating Cu anode, 30 kV, 100 mA and Ge(111) crystal. Thicknesses of the layers were chosen from 10 to 500 nm.

**Fig. 9** Escape probability of electrons in Cu in dependence on the depth of their release from an atom with regard to the surface of the specimen and their kinetic start energy.
The various kinds of electrons differ by the probability of their occurrence and their kinetic start energy. Inelastic collisions in the specimen are responsible for a systematic decrease of kinetic energy. The escape probability describes the probability of electrons to reach from the point of their origin the surface of the specimen and to leave from there. The escape probability depends on the specimen, the depth from where the electron starts and on its kinetic start energy. Fig. 9 gives the escape probability of pure Cu. The curves are the results of Monte Carlo calculations. Start directions of the electrons were chosen arbitrarily. From these considerations follows that the assumption of an exponential law for signal and thickness as it was used together with the discussion of Figs. 7 and 8 can be only a first approximation. Further considerations and results of experiments on escape probabilities have been published by numerous authors.

Fig. 10 Measured TEY responses of thin Cr layers on Si wafers. Cr-K jumps are from layers with thicknesses starting from 0.5 nm. The left hand spectra are from layers without an additional coverage. The right hand spectra are from identical Cr layers with an additional Al overlayer of 20 nm.
Fig. 10 gives the results of measurements which were performed on thin Cr layers on Si substrates. The TEY responses are an evidence for the detection limit of TEY. Layers of less than 0.5 nm can be detected. Thus, TEY is a method which can be applied to submonolayers up to layers of thicknesses less than 100 nm. The excellent detection limits of TEY recommend an application of TEY to thin layers. Additionally, TEY offers an interesting application to the quantification of buried layers. The second series of measured TEY responses of Fig. 10 are from Cr layers on Si substrates with an Al overlayer of 20 nm. The well pronounced thickness dependence of the Cr-K jump allows for quantitative investigations of buried layers.

A comparison between TEY and XRFA asks also for the differences in the theoretical description of the signals. The theory of the fundamental parameter approach of quantitative XRFA deals with primary and secondary excitation of characteristic radiations of the investigated specimens. In TEY similar algorithms can be used. But the following essential differences have to be considered:

1. Electron emission is caused by photoelectric absorption of monochromatic x-radiation in the specimen. Photoelectrons and in the course of the relaxation process Auger electrons are emitted. The probability of Auger electrons increases with decreasing fluorescence yield and decreasing atomic number of elements. Most of the emitted electrons are Auger electrons from their origin. This explains the decreasing elemental sensitivity of XRFA and the increasing elemental sensitivity of TEY with decreasing atomic number.

2. The original kinetic energy of the electrons decreases due to inelastic collisions in matter. Most of the electrons do not reach the surface of the specimen and the kinetic energies of those electrons leaving the surface form a continuous spectrum. The escape of electrons is determined by escape probabilities.

3. All atomic levels with binding energies less than the considered photon energy contribute to the resultant electron emission. For this reason, secondary excitation is not only restricted to excitation from one chemical element to another. Characteristic x-radiation of a chemical element causes also electron emission from atomic levels of the same element.

4. Fig. 11 gives examples of computed relative Cu-K\textalpha intensities and relative Cu-K jumps of two binary Cu-alloy systems. The Cu-Co response of XRFA shows the strong influence of matrix absorption of Cu-K\textalpha radiation in Co and the Cu-Ga response the enhancement by Ga-K radiations. Both contributions do not exist in TEY. The responses of TEY jumps versus composition are influenced by photoelectric absorption of incident x-radiation and by the density of the specimen under investigation. This explains the nearly linear TEY responses of Fig. 11. The linear responses recommend an application of TEY to quantitative analysis of just a single element in multielement specimens.
Fig.11 Comparison of computed XRFA and TEY calibration curves of binary Cu alloys.

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