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SI TRACEABLE CHARACTERISATION OF NANOMATERIALS BY X-RAY SPECTROMETRY

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1. *ABSTRACT*

The development of new materials and the assessment of nanomaterials require the correlation of the materials' functionality or toxicity with their chemical and physical properties. To probe these properties, analytical methods that are both sensitive and selective at the nano- and microscales are required. The reliability of most analytical methods is based on the availability of reference materials or calibration samples, the spatial elemental composition of which has to be as similar as possible to the matrix of the specimens of interest. However, there is a drastic lack of reference materials in particular at the nanoscale. The Physikalisch-Technische Bundesanstalt (PTB) addresses this challenge by means of a bottom-up X-ray analytical method where all instrumental and experimental parameters are determined with known contributions to the uncertainty of the analytical results. This first-principle based approach does not require any reference materials but a complete characterisation of the analytical instruments' characteristics and, in addition, knowledge on the X-ray fundamental parameters related to the elements composing the sample. In order to reveal more reliable FP data in line with recent FP roadmap recommendations, PTB has been developing and using calibrated instrumentation, both energy- and wavelength-dispersive X-ray spectrometers, in conjunction with well-known synchrotron radiation of high spectral purity. Examples of recent PTB works on different FP determinations mostly of technologically relevant elements are given. Synchrotron radiation based X-ray spectrometric methods allow for the variation of the analytical sensitivity, selectivity, and information depth needed to effectively reveal the spatial, elemental, and chemical specimen parameters of interest. Examples of particle characterisation, interfacial speciation, elemental depth profiling, as well as layer composition and thickness characterisations in advanced materials and nanostructures as well as for in-situ conditions are be given.

2. *INTRODUCTION*

The development of new materials and the assessment of nanomaterials requires the correlation of the materials' functionality or toxicity with their chemical and physical properties. These requirements are driven by the steadily increasing needs for the integration of different technological processes in one device or spatially closely coupled devices calling for complete understandings of these processes and the related device functionalities. To probe the related chemical and physical properties reliably, analytical methods that are both sensitive and traceable at the nano- and microscales are required [1]. The reliability of most analytical methods is based on the availability of reference materials or calibration samples, the spatial elemental composition of which has to be as similar as possible to the matrix of the specimens of interest. However, there is a drastic lack of reference materials, in particular at the nanoscale. This considerably affects the quantification reliability of most analytical methods, as reference materials are used to compensate for missing knowledge on instrumental or experimental parameters of the analytical technique. In many categories (such as film thickness, nano-objects or nanoparticles, depth profiling resolution) the number of existing nanoscaled reference

materials [2] corresponds to the number of new nanomaterials introduced in the market each month. The German National Metrology Institute - Physikalisch-Technische Bundesanstalt (PTB) addresses this challenge of missing nanoscaled reference materials by means of a bottom-up, International System of Units (SI)-traceable X-ray analytical method, X-ray spectrometry (XRS), where all instrumental and experimental parameters are determined with known contributions to the uncertainty of the analytical results [3]. This first principle-based approach in XRS does not require any reference materials, but a complete characterisation of the analytical instruments' characteristics and, in addition, knowledge on the X-ray fundamental parameters [4] related to the elements composing the sample. The characterisation of instrumental and experimental parameters can be reliably performed using X-ray radiometry, thus metrology of X-ray radiation, allowing for the calibration of components of X-ray instruments by comparing them to primary source or detector standards [5].

During the last decade, an international consortium of key players in academics, the industry, and metrology organised a continuously updated X-ray fundamental parameters roadmap [6]. Current fundamental parameter-related research aims at improving the knowledge on fundamental parameter data by means of experimental and theoretical methods by novel instrumentation, specimens, and algorithms [4, 7, 8] allowing for a reduction in analytical uncertainties of XRS for both chemical traceability and SI traceability. Synchrotron radiation-based X-ray spectrometric methods allow for the variation of the analytical sensitivity, discrimination capability, quantification reliability, and information depth needed to effectively reveal the spatial, elemental, and chemical specimen parameters of interest. SI-traceable XRS has been successfully applied as a reference measurement technique to determine surface contamination [9] on flat substrates, perform particle characterisation with respect to elemental or species composition, and enable interfacial speciation [10, 11] or elemental depth profiling of nanolayered systems [12]. For process-oriented applications or other analytical methods, calibration samples could be qualified with respect to layer composition and thickness in advanced materials [13], sur-face functionalisation [14, 15] or biomedical materials [16, 17]. Recent instrumental achievements provide access to liquids [18, 19], liquid-solid interfaces and even the in-situ and operando elemental analysis and chemical speciation of nanoscaled battery materials [20]. Furthermore, X-ray spectrometry under grazing incidence is capable of revealing analytical and dimensional information from layered systems, nanostructures and particles deposited on surfaces [21].

3. REFERENCE-FREE X-RAY FLUORESCENCE ANALYSIS

The continuing development of analytical methods based on reference-free X-ray spectrometry (XRS) and related instrumentation by the Physikalisch-Technische Bundesanstalt (PTB), Germany's national metrology institute, is enabled by the use of well-characterised X-ray sources and detectors as well as by well-known experimental arrangements allowing for the determination of atomic fundamental parameters. For radiometric purposes, PTB operates

several well-characterised beamlines for monochromatised synchrotron radiation at the 1.7 GeV electron storage ring BESSY II. Two of these beamlines, a plane grating monochromator (PGM) beamline for undulator radiation and a four-crystal monochromator (FCM) for bending magnet radiation, serve as excitation sources for reference-free XRS. Employing calibrated photodiodes in conjunction with monochromatised synchrotron radiation of a preselectable intensity, i.e., by varying the stored electron beam current at BESSY II, the absolute counting efficiency and response behaviour of energy-dispersive X-ray detectors, such as a Si(Li) or SDD detector, can be determined experimentally. With respect to the XRS beam geometry, special attention has to be paid when defining the angles of incidence and observation as well as the solid angle of detection. The methodological development of XRS at PTB is, among other issues, dedicated to high-end investigations in the R&D of semiconductor samples related to industrial applications requiring reference-free methods, in particular for new materials where not enough appropriate reference materials are available. The use of monochromatised synchrotron radiation at BESSY II has led to developments in the non-destructive investigation of wafer surface contamination, speciation and nanolayered materials by reference-free XRS.

Figure 1 shows the principal arrangements in reference-free X-ray spectrometry: total-reflection X-ray fluorescence (TXRF) at very shallow angles of incidence, grazing-incidence X-ray fluorescence (GIXRF) at intermediate angles of incidence, and convention-al XRF at rather high angles of incidence. In PTB's instrumentation for XRS, photodiodes are used to record the radiant power of the incident, transmitted or reflected beam.

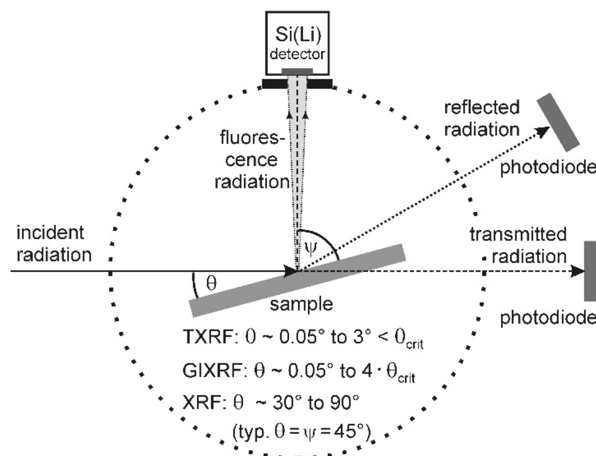

Figure 1. Typical arrangements for reference-free XRS employing monochromatised synchrotron radiation as the incident excitation radiation. The solid angle of detection is defined by a known diaphragm placed in front of the Si(Li)-detector at a given distance with respect to the centre of the sample. When detecting fluorescence radiation with one detector, the angle between the incident radiation and the fluorescence detection channel is 90°. When simultaneously detecting fluorescence radiation with two different detectors, normal incidence ($\theta = 90°$) and observation angles ψ of the detectors of 30°, 45° or 60° with respect to the sample surface, respectively, are chosen. θ_{crit} designates the critical angle of external total reflection at a flat sample surface.

If all relevant instrumental and atomic fundamental parameters are known, the concentration C_i of the element i in a homogeneous multi-elemental sample s of thickness T can be calculated without additional references using, for example, the following basic quantitation formula of X-ray fluorescence analysis:

$$C_i = \frac{P_i}{P_0 \tau_{i,E_0} Q \frac{\Omega_{det}}{4\pi} \frac{1}{\sin\Theta} \frac{1-\exp(-\mu_{tot,i}T)}{\mu_{tot,i}}} \tag{1}$$

where E_0 is the photon energy of the incident (excitation) radiation, $P_0 = S_0 / \sigma_{diode,E_0}$ is the radiant power of the incident radiation to be converted into the incident radiation intensity, S_0 is the signal of the calibrated photodiode measuring the incident radiation, σ_{diode,E_0} is the spectral responsitivity of the calibrated photodiode, θ is the angle of incidence with respect to the sample surface, E_i is the photon energy of the fluorescence line l of the element i, R_i is the detected count rate of the fluorescence line l of the element i, ε_{det,E_i} is the detection efficiency of the Si(Li)-detector at the photon energy E_i, $P_i = R_i / \varepsilon_{det,Ei}$ is the intensity of the fluorescence line l of the element i, τ_{i,E_0} is the photo electric cross-section of the element i at the photon energy E_0, $\mu_{S,E}$ is the absorption cross-section of the sample s at the photon energy E, $\mu_{tot,i} = \mu_{S,E_0} / \sin\theta + \mu_{S,E_i} / \sin\psi$ with ψ being the angle of observation with respect to the sample surface, Ω_{det} is the effective solid angle of detection defined by both a calibrated aperture placed at a well-known distance from the sample in front of the Si(Li)-detector and the foot print of the excitation radiation on the sample surface, ω_{Xi} is the fluorescence yield of the absorption edge Xi (of the element i), $g_{l,Xi}$ is the transition probability of the fluorescence line l belonging to the absorption edge Xi, j_{Xi} is the jump ratio at the absorption edge Xi , and $Q = \omega_{Xi} g_{l,Xi} (j_{Xi} - 1) / j_{Xi}$. In the case of flat samples excited at shallow incident angles, the modulation of the incident radiant power by the X-ray standing wave (XSW) intensity [10] has to be included as an additional factor. Secondary and tertiary excitation channels within a homogeneous layer or bulk sample as well as intra-layer excitation and absorption effects can be likewise included as indicated in detail in the literature [22].

When part of the experimental parameters such as the spectral distribution of the excitation radiation, e.g., in case of an X-ray tube, or the efficiency of the detectors employed are not known well enough, one may try to compensate this lack of a priori knowledge by using appropriate reference materials or calibration samples. The reliability of this reference-based quantitation approach strongly depends on the use of reference materials that should be as similar as possible to the specific samples to be analysed, in particular with respect to the specimen matrix. As this requirement can often not be fulfilled easily, various techniques to correct for matrix effects have been developed and validated. In the case of inhomogeneous matrices, analytical expressions for the elemental concentrations can only be given when a complete description of the spatial distribution of the main matrix constituents can also be given. Otherwise, Monte Carlo based simulations may contribute in overcoming a lack of sufficient a priori knowledge concerning the spatial distribution of main matrix elements or, when including multiple scattering effects for which analytical expressions are more difficult to deduce, in the spectral decomposition.

The current work describes the basic requirements and fields of applications of reference-free XRS, i.e., when all relevant experimental parameters are well known (Fig. 2). This includes, of course, sufficient a priori knowledge of the spatial distribution of the main matrix constituents as is the case for homogeneous and layered samples. Depth gradient variations in the matrix concentrations may also be dealt with when known a priori. In multi-elemental samples the radiation of one element can enhance the fluorescence intensity of another. This is referred to as secondary fluorescence. Taking this effect into account appropriately is crucial for producing correct results in quantitative X-ray fluorescence analysis. This is especially relevant for thin layered samples, for which the individual mass depositions of each element in each layer are to be determined. If the respective densities are known, this knowledge then can be converted into corresponding layer thicknesses.

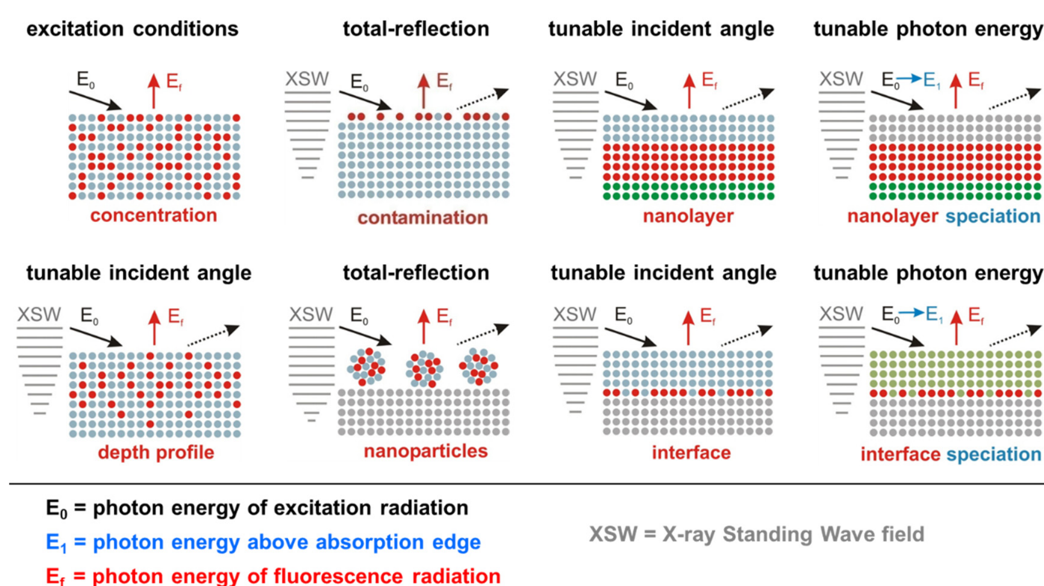

Figure 2. Different arrangements for reference-free XRS employing monochromatised synchrotron radiation as the incident excitation radiation. The analytical sensitivity and information depth can be tuned by means of appropriate operational parameters. When tuning the excitation radiation across the absorption edge of a main matrix element chemical binding state information can be revealed by X-ray absorption spectrometry.

Many new materials, e.g., in the semiconductor industry, are essentially thin layered samples at the nanoscale. Since appropriate reference materials are often not available, a reference-free approach based upon SI traceability might be the method of choice. The theoretical tools to calculate the required fluorescence intensities for the quantification algorithms are well-known and can be found in the literature [22]. Recent works at PTB aim on investigating the validity of these higher-order algorithms for selected thin layered samples, consisting of multiple transition metals with thicknesses in the low µm range. For these samples, the contribution of secondary excitation fluorescence can easily exceed 20 %, depending on the elements involved,

the spatial composition and dimensions of the layered system, the excitation energy and the angle of incidence. The calibrated instrumentation and the reference-free fundamental parameter approach [3] allow for a direct validation of the computed theoretical intensities with measured intensities. There is also a strong need in the medical device industry to decrease failure rates of biomedical devices by reducing the incidence of defect structures and contaminants during the production process. The detection and identification of defect structures and contaminants is crucial for many industrial applications. The present study exploits reference-free XRF analysis as an analytical tool for the traceable characterisation of surface contaminants of medical devices, in particular N,N'-ethylene-bis(stearamide), an ubiquitous compound used in many industrial applications as a release agent or friction reduction additive. Reference-free XRF analysis as primary method has been proven to be capable of underpinning all other applied methods since it yields the absolute mass deposition of the selected N,N'-ethylene-bis (stear-amide) contaminant whilst X-ray absorption fine structure analysis determines the chemical species. Ambient vibrational spectroscopy and mass spectroscopy methodologies such as Fourier transform infrared, Raman, and secondary ion mass spectroscopy have been used in this systematic procedure providing an extensive range of complementary analyses. A calibration procedure was developed using specially designed and fabricated model systems varying in thickness and substrate material [16]. Furthermore, typical real medical devices such as both a polyethylene hip liner and a silver-coated wound dressing have been contaminated and investigated by these diverse methods, enabling testing of this developed procedure. These well-characterised samples may be used as calibration standards for bench top instrumentation from the perspective of providing traceable analysis of biomaterials and surface treatments.

4. GRAZING INCIDENCE X-RAY SPECTROMETRY

During the last decades total-reflection X-ray fluorescence analysis, or TXRF, became one of the most powerful and cost competitive techniques for surface chemical and trace element analyses [22]. Tuning the angle of incidence across the critical angle of total external reflection, the composition of thin layered systems of low surface and interface roughness can be probed by means of the induced X-ray standing wave (XSW) field [10]. The dimensions of the XSW field intensity are employed as a nanoscaled sensor in this grazing-incidence XRF, or GIXRF, technique [13]. TXRF and GIXRF have successfully demonstrated their analytical capabilities in various modern applications to bio- and nanotechnologies [12, 16, 17, 21] involving minute sample amounts, surface functionalisations, nanoparticles and nanostructures. Even information about species mass depositions and the related chemical binding states [10, 11] can be revealed when using tuneable excitation radiation. A reliable and non-destructive metrology of in-depth elemental distributions and dimensional parameters of nanoscaled layer systems and 3-dimensional nanostructures is an essential topic in many fields of research, especially the semiconductor industry. With the decreasing minimal feature sizes and increasing complexity of the used structures, also the metrological challenges for a reliable characterisation of such structures increase. As they must be characterized both with respect to their dimensional and

elemental distribution parameters, a further development of the current analytical techniques is required. A combined grazing incidence X-ray fluorescence (GIXRF) and X-ray reflectometry (XRR) approach is capable of contributing to the in-depth and the dimensional characterisation of such nanoscale materials. When combining XRR with reference-free GIXRF [13], a direct access to the mass depositions (*ρd*) of the materials of interest is provided. This allows for a significant reduction of the degrees of freedom within the combined GIXRF-XRR modelling and thus improves the characterisation reliability of the methodology. The combined reference-free GIXRF-XRR approach has been applied for the in-depth analysis of thin nanolaminate stacks of Al_2O_3- and HfO_2-layers with total thicknesses in the sub-10 nm regime. For the GIXRF modelling of these nanostructures a novel approach for the calculation of the X-ray standing wave field intensity distributions [21] is necessary.

5. HIGH RESOLUTION X-RAY SPECTROMETRY

The complete understanding of the functionality of battery components requires the correlation with underlying physical and chemical properties, which is the challenge for most analytical methods due to a lack of reference materials. Lithium sulphur (Li-S) batteries are promising candidates for improved batteries offering up to 5 times higher capacity than conventional lithium ion batteries. The main degradation is caused by polysulphides formed during cycling, which are soluble in the electrolyte solution. For a better understanding of this process in-situ and operando characterisation techniques are required [20]. PTB used CR-2032 coin-cell formed Li-S batteries with DOL/DME (1:1 wt%) 1 Mol TFSI electrolyte modified with thin cathode current collector and thin window enabling the transmission of excitation and fluorescence radiation. SI traceable X-ray spectrometric measurements were performed using radiometrically calibrated instrumentation in the PTB laboratory at BESSY II synchrotron radiation facility. By means of operando near edge X-ray absorption fine structure (NEXAFS) spectrometry at the S--K edge recorded during galvanostatic cycling with potential limitation (GCPL) measurements different sulphur species in the cell can be determined. For 8 full charge/discharge cycles (0.1 C) operando sulphur K-edge NEXAFS could be registered. After a spectral deconvolution the different sulphur species and their behaviour over time were analysed. While for the first cycles a reversible formation of polsulphides is visible further cycles show a steady increase of polysulphides due to the solubility in the electrolyte solution and, thus, the loss of cathode active material and capacity fading. The investigation of polysulphides for different states of charges (SOC) and state of health (SOH) enables a deeper understanding of the main degradation process. This information helps to improve the battery system by modifying its materials, e.g., with binder components or by choosing an optimal (dis-)charge current. The simple set-up enables also investigations from the anode side. In addition, the set-up can be adapted for different types of batteries with other active materials, e.g., NCM Li-ion batteries.

Depending on the specific valence states of compounds high resolution X-ray emission spectrometry (XES) may provide valuable complementary information to XAFS. XES can equally contribute to the further development of complex nanomaterials with distinct chemical properties. Also in the field of catalysis, the identification and quantification of active sites is important for a more thorough understanding of catalytic systems. Using a physically traceable X-ray analytical approach based on calibrated instrumentation and the knowledge of atomic fundamental parameters, absolute elemental and species mass depositions or concentrations can be determined without the need for any reference material or calibration standards. For this purpose PTB build a calibrateable and compact high-resolution wavelength-dispersive X-ray spectrometer [23] for XES in the photon energy range of 2.4 keV to 19.0 keV. Using two full-cylindrical highly annealed pyrolytic graphite (HAPG) crystals as dispersive elements in modified von-Hamos geometry, a large solid angle of detection resulting in high detection efficiency is realised while achieving a moderate to high resolving power. HAPG is a synthetic type of carbon that forms mosaic crystals and can be mounted to substrates with small radii of curvature down to 50 mm. Although the peak reflectivity is smaller than for perfect crystals, the crystal mosaicity results in a rather high integrated reflectivity. The instrumental characterisation of the spectrometer included the achievable energy resolution and efficiency as well as the spectral response as a function of experimental parameters. Furthermore, the chemical speciation capability of the device has been demonstrated on the basis of different transition metal compounds. The calibration of the instrumental response of the wavelength-dispersive X-ray spectrometer enables an accurate determination of binding state related structures in X-ray spectra, thus enabling reliable identification and discrimination capabilities.

Synchrotron radiation (SR) based scanning X-ray spectroscopy (XRS) can determine both elemental concentrations and chemical binding states with high spatial resolution down to the nanoscale. At SR facilities, there are currently only a few dedicated scanning X-ray microscopes that offer XRF analysis in combination with scanning transmission X-ray microscopy (STXM). A novel kind of vibration compensating XRF set-up [24] have pushed the spatial resolution towards the 100 nm regime. With the advent of UHV-compatible piezo stages with nanometre resolution, it became possible to mount optical elements in a compact manner on a single platform. Relevant parts of any external vibrations can be compensated for by such a single platform. The layout of its stages and related holders is to ensure amplitudes of relative vibrational movements to be smaller than the absolute ones by avoiding any resonance frequencies. PTB realised this approach in a compact set-up to align diagnostics, zone plates, order sorting apertures (OSA) and samples on a single mounting plate. This plate was mounted on a sample manipulator of an UHV XRF instrument. Its overall size offers versatile areas of operation as the compact set-up can be readily inserted in a wide range of XRF chambers through their load-locks. The optical elements of the scanning X-ray microscope consist of an Au zone plate with an 50 µm integrated central stop and an independent 50 µm OSA. All measurements were carried out with photon energy of 1,500 eV at PTB’s plane grating monochromator beamline for undulator radiation at BESSY II. Two objects were used to examine the performance of the novel type of scanning nm-XRF microscope. The test object for STXM was

a Siemens star on a Si_3N_4 membrane completely covered with a 133 nm thick layer of W, while for the fluorescence experiments we chose a silicon wafer with an alternating Ge-Si-wafer bar test structure. The smallest structures (approximately 100 nm) were clearly resolved in transmission while the resolution was slightly larger in XRF mode. Here, the Ge-Si-sample was measured at an angle of incidence of 60° with an energy-dispersive X-ray silicon drift detector (SDD) calibrated by PTB. The highest spatial resolution achieved in initial experiments was in the range of 130 nm to 140 nm, which is in line with the probed sample dimensions. Follow-up experiments are going to be focussed at traceable XRS of appropriate and even smaller test structures.

6. DETERMINATION OF ATOMIC FUNDAMENTAL PARAMETER

The quantitative analysis of X-ray fluorescence and electron induced X-ray spectroscopic methods requires good knowledge of the atomic fundamental parameters (FP) and optical constants involved. In addition, the lack of adequate reference materials and calibration samples, in particular at the nanoscale, reliable quantification schemes in X-ray fluorescence analysis and related methods call for a high accuracy of the X-ray fundamental parameters. However, the respective uncertainties of available tabulated data are usually rather large, especially for low-Z elements or L- and M-shell fluorescence lines. In order to address this issue, different methods for experimental FP determinations have been developed, validated and applied at the PTB. Those activities on the experimental determination of X-ray fundamental parameters cover the determination of low-Z fluorescence yields, subshell photo-ionisation cross-sections and Coster-Kronig factors [25]. Many data sets widely are being used in analytical applications such as XRF where subshell or partial photo-ionisation cross-sections (PCS) are derived from the total PCS by applying constant (energy independent) jump ratios [5]. Major X-ray equipment manufacturers widely use jump ratio values in their quantification algorithms and also the International Union of Pure and Applied Chemistry proposes the use of constant ratios in a standard reference guide. The ratios are defined by the jump height of the mass absorption coefficient at the respective absorption edge and are independent of the photon energy. The ratios are then used to subdivide the total PCS into the contributions of the various subshells (fixed jump ratio approximation). As Ebel indicated by comparing available data sets, this produces consistent results for the K-shell PCS and is rather questionable for the -L and M-subshells. Close to the L-absorption edges both approaches deliver similar results (by definition), but they differ significantly with increasing photon energy. As the PCSs have a direct impact on measurands such as the amount of substance, both the correct approach and values of PCS data need to be experimentally confirmed (Fig. 3). Meanwhile the energy dependent slope of these coefficients could be confirmed experimentally (Fig. 4) [4]. These coefficients were calculated theoretically by Scofield, and carefully evaluated and implemented by Ebel.

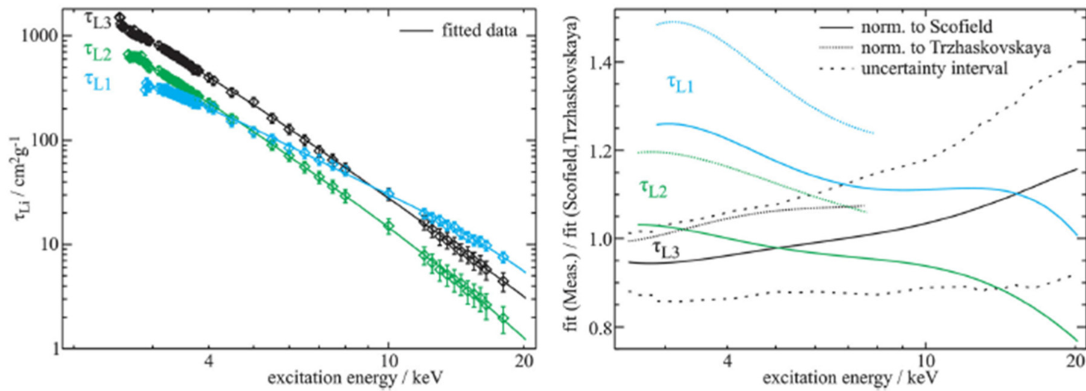

Figure 3. Experimentally determined PCS for the three Mo-L subshells (left) and the comparison to different calculated data sets (right) [4].

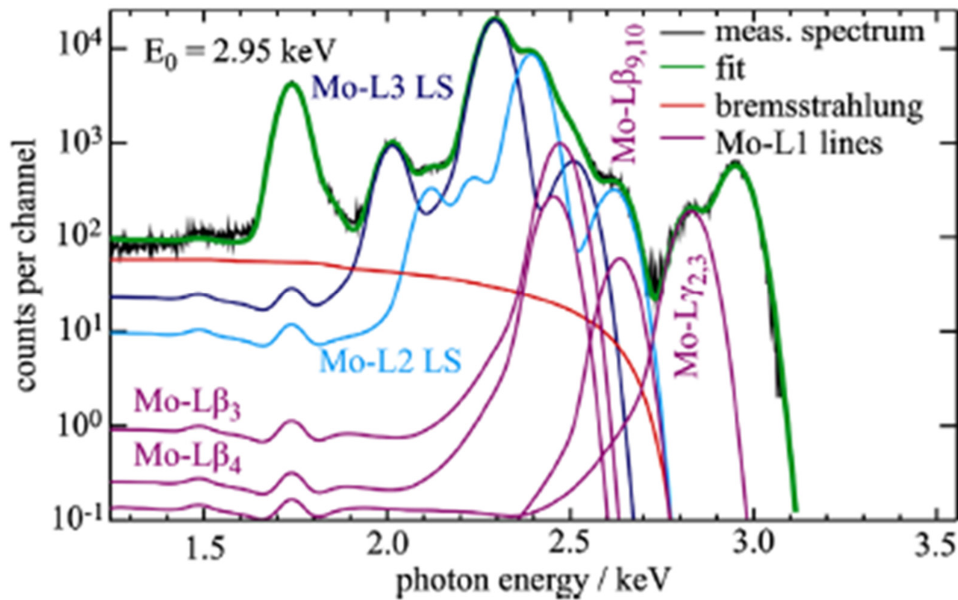

Figure 4. Response function based deconvolution of a Mo layer XRF spectrum for each L-shell used for the experimental determination of Mo-L PCS [4].

The determination of fundamental parameters (FP) for L-edges is an important part of reliable, reference-free quantitative XRF [3]. In order to reduce the uncertainties of the FP, transmission measurements of the samples have to be performed thus allowing to experimentally determining self-absorption correction factors. For reference-free XRF with lower excitation energies, the uncertainties of the fundamental parameter associated with L-edges are crucial for the total uncertainty of the quantification, especially for excitation energies above the L1-edge of the respective element. The fluorescence yields and Coster-Kronig transition probabilities for the L-edges of Ga were determined with considerably reduced uncertainties [26]. Due to the high absorption of radiation in the soft X-ray range, it is necessary to reduce the thickness of the

samples for transmission measurements. Here, a nominal 300 nm thin GaSe layer was deposited on a thin silicon-nitrate window for measuring both the transmission and the fluorescence intensities simultaneously in order to perform absorption correction without having to rely on literature database values of the mass attenuation coefficients. In order to reduce the uncertainty of the spectral deconvolution, a silicon drift detector (SDD) with an optimised energy resolution was employed. The measurements were carried out at the plane grating monochromator beamline in the PTB laboratory at BESSY II using monochromatised undulator radiation and calibrated instrumentation [3].

New measurements of mass attenuation coefficients were also carried out by the French National Metrology Institute Laboratoire National Henri Becquerel (LNHB), which took the advantage of using tuneable monochromatic radiation at SOLEIL synchrotron radiation facility, on the METROLOGIE beamline and using specific procedures. Within the frame of different institutional and industrial metrology research projects, the LNHB and partners studied several elements from photon energies as low as 100 eV up to 35 keV; special care was taken to ensure reliable uncertainties [8, 27]. The results of some of these collaborative studies do not agree with data previously published by other groups within their respective uncertainties.

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