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Abstract

The knowledge of atomic fundamental parameters such as mass attenuation coefficients or fluorescence yields with low uncertainties, is of decisive importance in elemental quantification involving X-ray fluorescence analysis techniques. Several databases providing the mass attenuation coefficients are accessible and frequently used within a large community of users. These compilations are most often in good agreement for photon energies in the hard X-ray ranges. However, they significantly differ for low photon energies and around the absorption edges of the elements. Mass attenuation coefficients of several elements were determined experimentally in the photon energy range from 100 eV to 35 keV by using monochromatized radiation at the SOLEIL synchrotron (France). The application of high-accuracy experimental techniques resulted in low uncertainty mass attenuation coefficients. The results are compared with tabulated data.

1 Introduction

A wide range of technical fields using X-ray methods to probe atoms need a reliable knowledge of atomic fundamental parameters with low uncertainties. Indeed, elemental quantification involving X-ray fluorescence analysis techniques relies on databases of mass attenuation coefficients, fluorescence yields and Coster-Kronig factors, line intensities, etc. For example, several databases providing the mass attenuation coefficients are accessible and frequently used within a large community [1, 2, 3, 4]. These compilations are based on theoretical approaches together with selected experimental data and are most often in good agreement for photon energies in the hard X-ray range ($E > 20$ keV). However, they significantly differ one from the other for low photon energies and around the absorption edges for most elements. The lower the energy, the more difficult the transmittance measurements, which led to a poor number of values being published in the literature. This explains why compilations based on measured values are so difficult to perform and why they rarely match with theoretical calculations below 1 keV. It must be noted that experimental determination of other parameters, such as fluorescence yields, often use the mass attenuation coefficients as a pre-requisite and therefore, their uncertainties are propagated, leading to large uncertainties that can be critical in some applications.

The Laboratoire National Henri Becquerel (LNHB), the French metrology laboratory for ionizing radiation, is developing dedicated X-ray spectrometry techniques with the aim to substantially improve the reliability of selected atomic parameters and their uncertainties. In the present paper, we give an overview of the methodology used to experimentally measure mass attenuation coefficients using thin foils. This methodology takes advantage of the accurate and independent measurement of the average mass per area of thin foil samples as well as the large X-ray spot available at the synchrotron source.

Several results were already published in the field [5, 6, 7, 8, 9, 10] for various elements. For every element, the K, L and M absorption edges were studied more carefully with adapted energy steps in order to describe the absorption fine structures if any. As soon as the results become available, they are proposed to users through a website.

2 A brief history of existing databases

Measuring mass attenuation coefficients has been a topic of interest since the very early XXth century. When the number of measurement values became large enough, first compilations and attempts of comprehensive interpolations were made. When calculations became possible with high-speed computers, early theoretical work delivered new sets of data, especially for elements difficult to measure. Saloman et al., in their comprehensive compilation of published experimental work [11] reported previous compilations of Allen in 1935, then Victoreen in 1949, but the first complete one which is still in use today is from McMaster in 1969 that was derived from measurements and theoretical calculations [12]. The compilation of Saloman starts with experimental data from Barkla and Sadler in 1907, and others up to 1988, and compared these values with relativistic calculations from Scofield [13, 14]. The theoretical calculations from Scofield of the photoionisation cross sections (the dominant effect in the low-energy range) were performed with a relativistic treatment of electrons moving in a Hartree-Slater central potential. In the presently available tables, coherent (Rayleigh) and incoherent (Compton) scattering cross sections are generally calculated as numerical integrations of the Thomson (1906) and Klein-Nishina (1929) formulas, respectively; however, relativistic calculations have been made available and should supplant these in future. The semi-empirical table from Henke [1] was also established from this list of papers, including a few others. More details are provided by Hubbell who made a general overview of compilations with historical remarks [15]. Later on, Elam [2] and Ebel [3] proposed new semi-empirical compilations based on the previous work. All semi-empirical compilations acknowledge the near linear relationship $\mu(E) = Exp(A_0 + A_1 \times Log(E))$ between absorption edges but for more accuracy Ebel uses instead a 5^{th} order polynomial fit and Elam uses a 3^{rd} degree spline fit.

Moreover, as presented in Figure 1, most of the measurements were carried out in the sixties and seventies. This implies that the experimental work were performed with X-ray sources of discrete energies and detectors with less accuracy than available today. Moreover, uncertainties were rarely mentioned, that is why Krause [16] could only make assumptions in trying to evaluate the associated uncertainties. Some recommendations have been made first in 1992 by Creagh et al. in [17] about new experimental approaches. Unfortunately, since the nineties, very poor interest was given to refine these studies from a metrological point of view. Nevertheless, some of these tables have been available on the internet through the CXRO website [18] for Henke tables [1] (Lawrence Berkely National Laboratory) or at the NIST for the calculations of Scofield presented by Berger [4]. Semi-empirical tables from Elam are distributed through the XRAYLIB library [19] and finally the comprehensive tables from Cullen, EPDL97, which was developed to meet the needs of users at Lawrence Livermore Laboratory, are available as an IAEA report [20]. More recently, Chantler et al. [21, 22] performed new measurements taking advantage of the latest experimental facilities and new theoretical calculations distributed on the NIST website to update such tables.

When looking at the interest of these measurements with respect to Z, the effort appears clearly inhomogeneous (Fig. 2). There are obvious reasons such as the difficulty to obtain self-supporting pure foils or the immediate interest for a specific element. However, this representation does not stand for the number of experimental data because some papers published many values while others provided only one value, it gives an approximate idea of the available data. If we except technetium ($Z = 43$) and promethium ($Z = 61$), which do not have any stable isotope, the interest focussed on light Z elements, transition metals or valuable metals (Ag, Pt, Au). Very little papers were found dealing with rare earth elements despite their metallic structure.

3 Methodology used at LNHB

The mass attenuation coefficient, (μ/ρ), is the parameter standing for the interaction probability of a photon beam in matter. According to the International Commission on Radiation Units and Measurements, "It is the quotient dN/N by ρdx where dN/N is the mean fraction of particles that experience interactions in traversing a distance dx in the material of density ρ" [23]. It depends on the material and the photon energy and includes the photo-absorption and scattering effects. The overall attenuation of a parallel and monochromatic photon beam at normal incidence to a target follows the Beer-Lambert law from which the mass attenuation coefficients can be derived:

$$\left(\frac{\mu}{\rho}\right) = -\frac{1}{\rho.x} \times \ln\left(\frac{I}{I_0}\right) = -\frac{A}{M} \times \ln\left(T\right) = \sum_i \tau_i + \mu_{Compton} + \mu_{Rayleigh} + \mu_{pair} + \mu_{triplet} \quad (1)$$

where I and I_0 are the transmitted and incident photon intensities respectively, ρ (in g.cm^{-3}) and x (in cm) are respectively the target density and thickness, (μ/ρ) is the energy-dependent mass attenuation coefficient in cm^2.g^{-1}, M is the mass of the sample in g, A its area in cm^2, T is the transmittance ratio, τ_i are the photoelectric absorption coefficients for the different subshells, $\mu_{Compton}$ and $\mu_{Rayleigh}$ are the incoherent and coherent scattering coefficients respectively, μ_{pair} and $\mu_{triplet}$ are the electron-positron pair production coefficient in the field of the nucleus and in the field of the atomic electrons respectively. These last two contributions occur only at photon energies above 511 keV which is not the case in this work. A transmission measurement procedure is a convenient way to determine the mass attenuation coefficient, using a monochromatic photon beam of low divergence. Consequently, the final uncertainty budget is linked to the target characteristics and the photon flux intensities. For reliable experimental results, i.e. with an uncertainty budget as low as possible, one has to know the photon beam intensity and characteristics with high accuracy. According to Nordfors [24], the transmission uncertainty is minimum for $2 < I/I_0 < 4$, which induces severe requirements on the sample thickness, typically $1\ \mu m$ for a photon energy of 1 keV. To cover the energy range from 100 eV to 30 keV, three complementary tunable monochromatic photon sources were used. Most of the experiments were performed at the Metrology beamline at the SOLEIL synchrotron, France, that includes two branches (XUV: from 100 eV to 1.8 keV and hard X-rays: from 3 keV to 35 keV). The gap between 1.8 keV and 3 keV was filled using the SOLEX source available at LNHB [25]. Contrary to the former experimental conditions, where only discrete energies were used, the availablilty of tunable monochromatic X-ray sources makes it possible to scan a continuous energy range, including the absorption edges. The scanning steps are between 10 and 50 eV on large energy ranges, but smaller steps of a few eV are imposed around the K, L, M or N absorption edges.

The hard X-ray branch at the SOLEIL Metrology beamline is composed of a double Si(111) crystal monochromator device whose Bragg angle is calibrated using the absorption edges of several metallic foils according to the corresponding energies reported by Deslattes [26]. The XUV branch is equipped with several focussing mirrors, three different variable line-spacing (VLS) gratings for the photon energy selection, filters and an order-sorter for minimizing the harmonics. The laboratory Source Of Low Energy X-rays (SOLEX) has already been used in recent works to derive the mass attenuation coefficients of several materials. This photon source consists of an X-ray tube and one bent crystal as monochromator, the photon energy calibration following the same procedure as detailed in [5]. The flux stability of this source is not as good as on a synchrotron radiation source, but its weak flux has the advantage of allowing the use of an energy-dispersive detector with specific selection of the energy of interest. Specific issues concerning the detector linearity or dead-time correction are taken into account as described in [27].

At the hard X-ray branch, the transmission measurements are performed using a beam collimated between 2×2 mm^2 and 3.5×3.5 mm^2 and the direct and transmitted photon beam intensities are recorded by means of an AXUV:Al photodiode whose dark noise is subtracted from all current values to derive an unbiased transmittance. The homogeneity of the samples are checked by making 2 dimensional scanning and by collimating the incident beam to a small spot of $200 \times 200\,\mu m$. This

procedure is only for checking the sample thickness, as we assume that the large spot areas used for transmittance measurement to be representative of the average thickness of the whole target. The measurement procedure was discussed in detail in [7], and so we estimated the uncertainty budget in the same manner.

Samples are thin foils chosen with the best possible purity, in general higher than 99.9% depending on the element. Some elements may be difficult to purify even with the best techniques. For example, zirconium is difficult to remove completely from hafnium as they have a similar chemistry. That is why hafnium cannot be found with less than ~ 3 % in mass of zirconium. To derive absolute values for the mass attenuation coefficients from equation (1), density and thickness must be known with the smallest possible uncertainty. However, it appeared to be difficult to measure a thickness in the range of micrometres or less with accurate techniques, thus at LNHB we chose to measure the mass per unit area. The mass is determined by weighing the sample with a calibrated microbalance used in a room whose ambient air hygrometry, temperature and pressure are controlled, leading to an absolute uncertainty of 9 µg at best. The area is measured with a vision machine consisting of a microscope with 2 calibrated stages and a picture analyser. Moreover, the transmittance in the low energy range are made using foils which are often to fragile to be handled by tweezers and their mass and area could not be measured independently. In this case we should rely on transmittance measurements undertaken with a thicker sample in the same energy range in order to hook up the transmittance and derive a mass per area, increasing the final uncertainty.

In order to derive the uncertainties associated with the measurements, equation (1) was derived according to all the influential quantities as mentioned in the "Guide to the expression of uncertainty in measurement" [28]. We included a correction factor $k_P = 1$ of which an uncertainty was derived to account for possible impurities [7]. To evaluate the uncertainty of the experimental mass attenuation coefficients, the uncertainty budget was evaluated using the following formula:

$$\left(\frac{u\left(\mu/\rho\right)}{\mu/\rho}\right)^2 = \left(\frac{u\left(M\right)}{M}\right)^2 + \left(\frac{u\left(A\right)}{A}\right)^2 + \frac{\left(\frac{u(T)}{T}\right)^2}{\left(\ln\left(T\right)\right)^2} + \left(\frac{u\left(k_P\right)}{k_P}\right)^2 \tag{2}$$

Depending on the photon energy and on the sample thickness, the influence of the transmittance (T) is variable on the total uncertainty. The influence of the purity was always calculated as a small contribution. For sample foils of which mass and area are directly measurable, we found that their contribution to the total uncertainty is about 0.1% each, the same order of magnitude was found for the purity. Finally the contribution of the uncertainty of the transmittance measurement is due to harmonics, stray light and flux stability and is the main contribution when T is large, but comparable to the other ones when small.

4 Comparison of mass attenuation measurements with EPDL97

Thirty two pure elements have been studied using the updated methodology, including values in the soft X-ray range, down to 100 eV (or even 70 eV for Cu in association with PTB) and up to 35 keV. New values are obtained with a relative combined standard uncertainty below 2%. We discussed in previous papers the determination of the mass attenuation coefficients for copper and zinc [7], nickel [8], germanium [29], tin [10] and bismuth [9]. As an example, values for silver are presented as they appear on the website for users on Figure 4. This example focussed on the values measured at LNHB around the L transition edges. The relative differences between the new measurements and tabulated values for several elements are presented in Figure 3. This figure shows the relative deviation in percent defined as follows:

$$\frac{\Delta\mu}{\mu} = \left\| \frac{\mu_{EXP} - \mu_{EPDL97}}{\mu_{EPDL97}} \right\| \times 100 \tag{3}$$

where μ_{EXP} stands for the presently measured mass attenuation coefficients and μ_{EPDL97} stands for values from the Cullen database [20], which has the largest energy range (from 1 eV to several GeV).

As expected, the larger deviations are found at photon energies lower than 1 keV but other differences are visible close to the transition edges. For energies between L and K transition edges, discrepancies as large as 5% can be found for transition metals.

5 Sharing the new data with the community: website

A website hosted by the LNHB is available to users, giving access to the new measured values as well as some practical tools (http://www.nucleide.org/Laraweb/Mu/). The user is first invited to choose an element of interest in the list of available ones: available elements are marked with a star, other ones are scheduled to be online. Three tools allow the user to obtain values from the measured data. Some examples of use are shown in Figures 4 and 5. The first one shows the mass attenuation coefficients with their uncertainties, as measured in a selected photon energy range (leaving this box empty retrieves all the available data). One can select to see a plot of the data, either in linear or logarithmic scale. The two other tools are built on the same model and perform calculations of the transmittance or thickness using the Beer-Lambert law. One can calculate several steps of transmittance for several thicknesses in a given energy range. Similarly, one can select the transmittance ratio to have an idea of the thickness needed in a selected energy range. All new values will be made available progressively for users on the website.

6 Conclusion

The use of new experimental facilities allowed to renew measurements of mass attenuation coefficients in a large energy range with well controlled uncertainties. The results are presented for 20 elements but measurements were also performed for 12 other elements, but either uncertainties or absolute values are not available yet. Using the methodology presented in this article, only 51 elements out of 81 (from hydrogen to bismuth, less technetium and promethium) can be measured using thin foils, the others are powders, liquids or gases and only compounds may be considered in the future. The new experimental data are made available for users through the LNHB website, on a dedicated page that will be enriched with further measured values; in the future it is also planned to include the derived atomic scattering form factors and complex index of refraction for practical use in X-ray reflection techniques.

Acknowledgments

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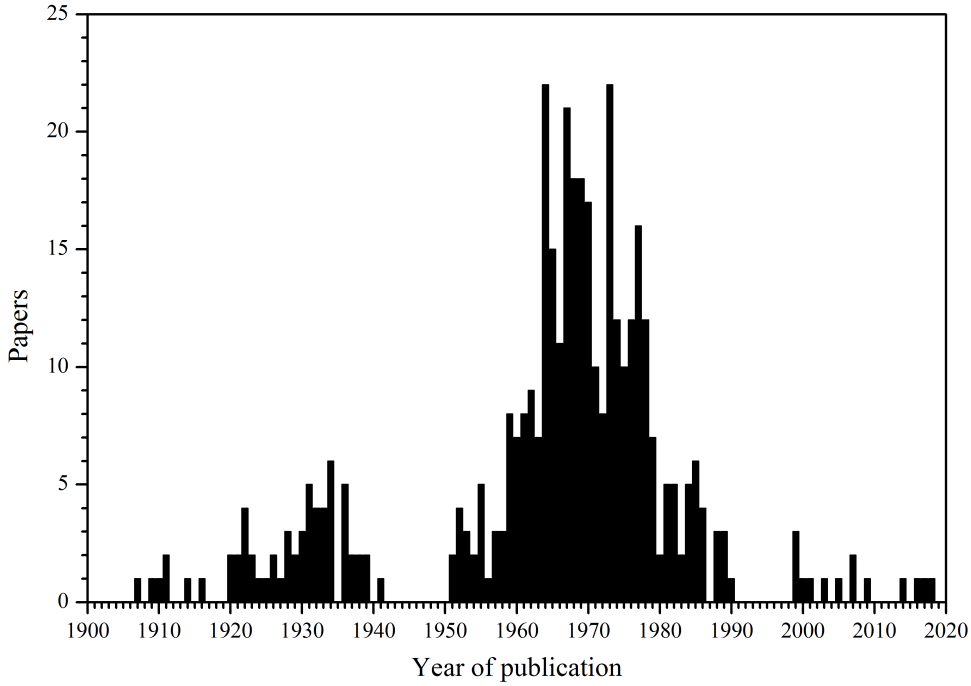

Figure 1: Number of published papers per year about mass attenuation coefficients measurements.

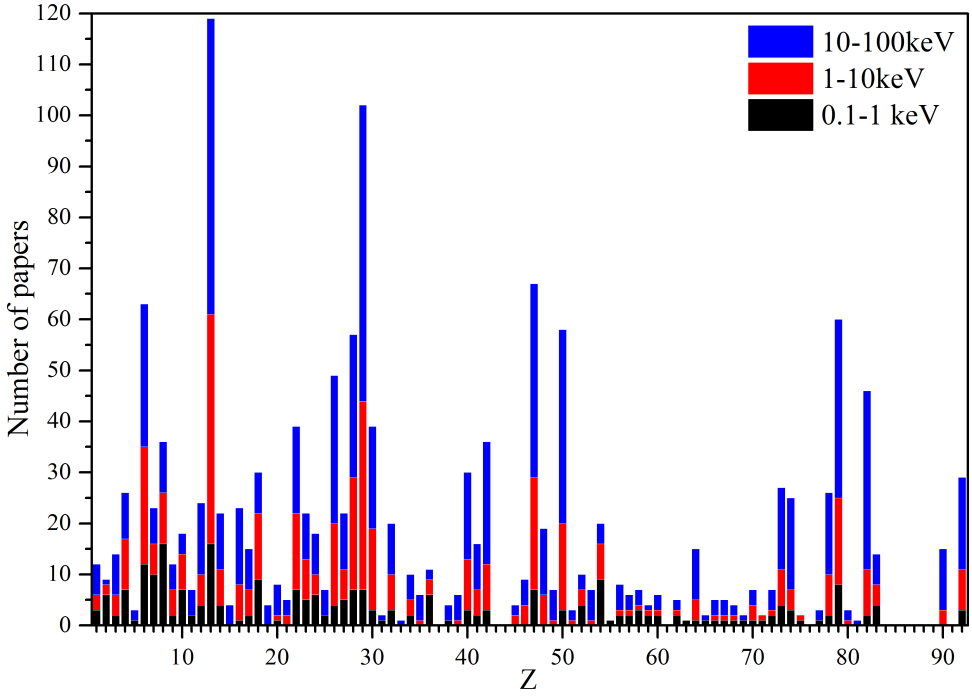

Figure 2: Number of papers per element publishing experimental values of mass attenuation coefficients.

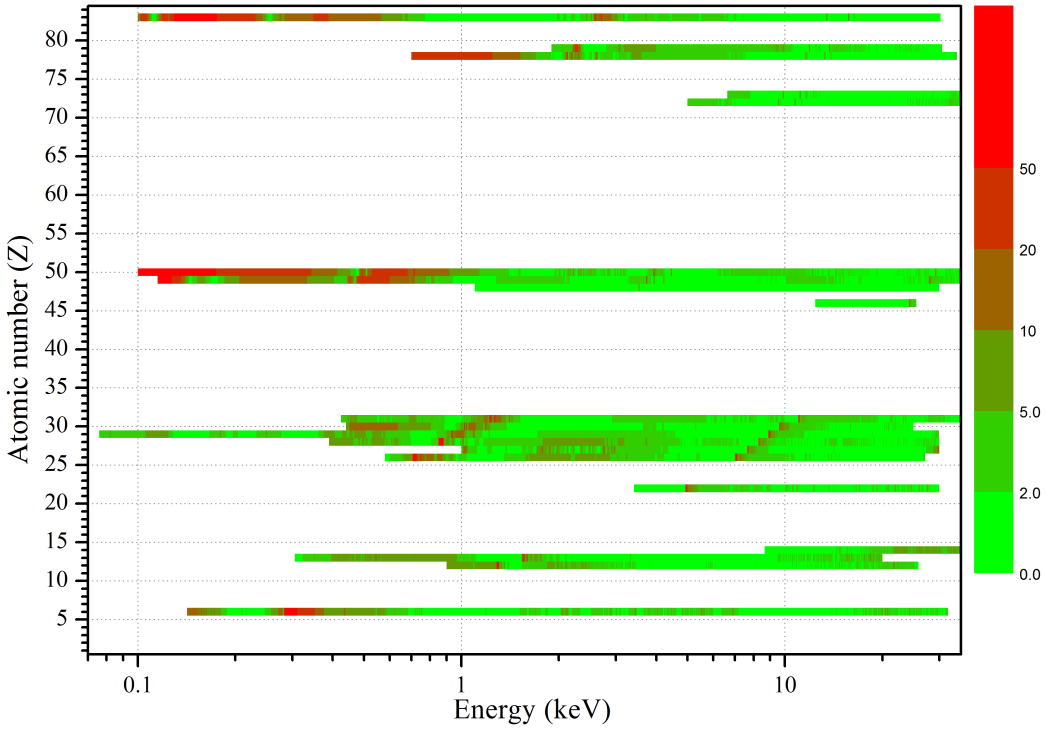

Figure 3: Comparison of measured mass attenuation coefficients of several elements with EPDL97 [20]. The color scale is in percent difference.

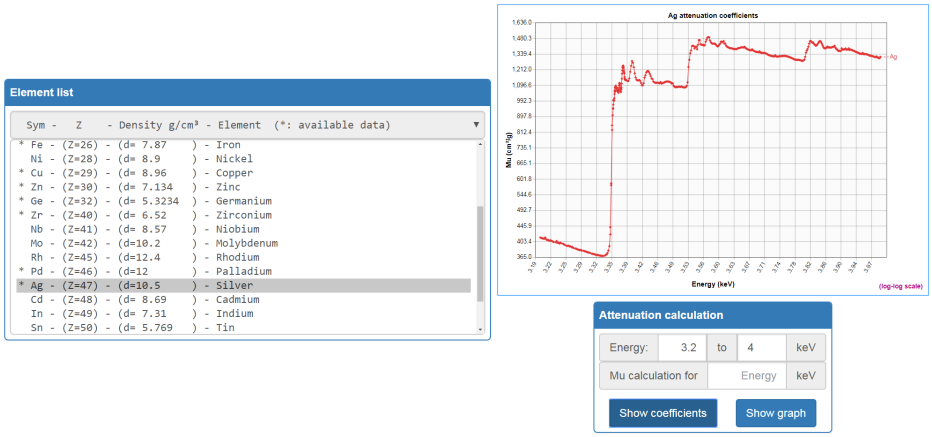

Figure 4: Example of the mass attenuation coefficients of Ag available at (http://www.nucleide.org/Laraweb/Mu/ on Ag close to the L absorption edges.

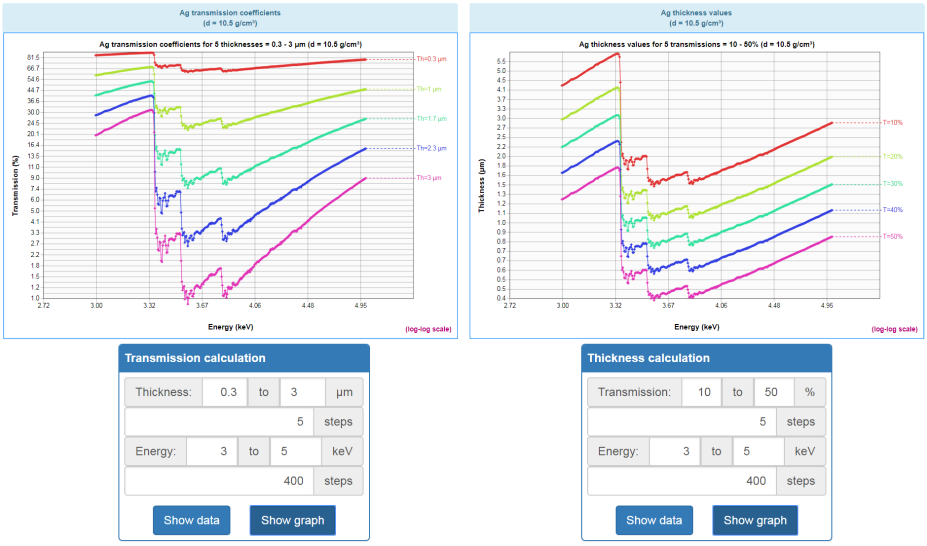

Figure 5: Example of the tools available at (http://www.nucleide.org/Laraweb/Mu/ on Ag close to the L absorption edges.