# Precision X-ray optics for fundamental interactions in atomic physics, resolving discrepancies in the X-ray regime

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**Abstract.** Reliable knowledge of the complex X-ray form factor ($\mathrm{Re}(f)$ and $f''$) is required for many fields including crystallography, medical diagnosis and XAFS studies. However, there are discrepancies between theory and theory, experiment and experiment and theory and experiment of 10% and more, over central X-ray energies. Discrepancies exist for most elements, despite claimed experimental accuracies of 1%. This paper summarises the current variation between experimental and theoretical results, and outlines key issues for obtaining experimental accuracies of 1% in critical wavelength ranges for selected elements to address these issues. This paper critically surveys available experimental data for attenuation coefficients and suggests a procedure for obtaining significantly higher accuracy measurements in the future.

## 1. Introduction

The complex form factor $f$ is the core parameter for all optical devices. It specifies refractive indices, scattering and attenuation coefficients, and hence the critical properties for mirrors, lenses, filters and coatings. As the photon energies increase, the complex form factor becomes more accessible to theoretical prediction on the basis of atomic physics and the atomic form factor (i.e. neglecting nearest neighbour interactions, phonon interactions and nuclear structure) (e.g. Chantler 1993).

This atomic form factor is used universally in X-ray optics and X-ray investigations. Crystallography depends on the unique structure factor amplitudes to determine sample elemental composition and distribution in space, i.e. to determine the crystal structure. Recent XAFS (X-ray absorption fine structure) investigations probe the critical region near the absorption edges where the form factor has a strong structure and rapid variation. One of the benefits of this new field of XAFS is the possible selective measurement of specific elemental distributions, and detailed information on bond lengths and the local environment of atoms (e.g. Sorensen *et al.* 1994).

Medical diagnosis is often considered an uncritical application of the form factor theory; but it has been well established that conventional techniques may overdose the patient, show poor contrast, or be characterized by purely empirical sampling of the parameter space (Chantler *et al.* 1996). In addition to these difficulties, new approaches which more critically use the form factor theory offer the possibility of much safer procedures (Nugent *et al.* 1996).

Because these applications are well established, researchers outside the field, and some users, have assumed that experiment and theory have converged with no further critical goals in this area. This assumption is seriously flawed for all elements, and in all energy regions. In fact, the most carefully and fully tested pure elemental species such as silicon, copper and gold are little better defined than the most inadequately understood samples.

This paper will discuss some key issues and observations behind the current dilemma, and some preparations towards a proper resolution of theoretical and experimental flaws.

## 2. Experimental and theoretical variability

The imaginary component of the atomic form factor is directly related to the photoelectric absorption coefficient $\mu_{\mathrm{PE}}$:

$$\mathrm{Im}(f) = f''(E) = f_2(E) = \frac{E\mu_{\mathrm{PE}}(E)}{2hcr_e} \tag{1}$$

Collections of experimental data for form factors are widespread, particularly for common elements such as silicon, copper, silver and gold over the central X-ray energies. This is directly related to databases of attenuation coefficients and total photon cross-sections as indicated (Saloman *et al.* 1988). The variation of the coefficient for a given element and energy is 10–30%. The effect of a 10% error is similar to a 10% error in the thickness of the sample, or a 10% error in the exponent of the probability of photo-absorption through a sample. This will, for example, be reflected in Bragg or Laue diffraction profile shapes or visibility of interference fringes (e.g. Chantler and Deslattes 1995). This variation seems almost independent of the year of the experiment, or the specification for high or low energy measurements.

Turning exclusively to measurements claiming high accuracy, i.e. of order 0.5% or 1%, we narrow the spectrum of measurements only slightly (e.g. Wang *et al.* 1992; Gerward 1989). Clearly a number of systematic error sources are not accounted for. As experimentalists, these (unknown) error sources represent an intriguing limitation to X-ray investigations of all types, and hence an issue of fundamental importance.

A first step would be to turn to a reliable theory and filter experimental results on this basis. There are several theoretical approaches to solving the quantum mechanical problems involved. Each has a range of applicability. Exact solutions for monatomic hydrogen or (at a simpler approximation) hydrogen gas are very poor indicators for the bound hydrogenic form factors observed in almost all relevant investigations. Recent general approaches are usually limited in terms of the single-electron excitation approximation, and the isolated atom approximation, but serve as powerful references for the experiment. Of these, two of the most recent and most comprehensive were developed by researchers in Australia (Chantler 1995; Creagh and McAuley 1995). Comparing these uncritically with other commonly used theoretical references (Saloman *et al.* 1988) reveals a surprising variation and uncertainty in the theory.

It is difficult to accurately assign uncertainty to these theoretical results, and the uncertainty varies dramatically across energy ranges for well-defined reasons. However, a figure of 0.1–1% or better has been quoted away from edges and in the medium energy range (Saloman *et al.* 1988; Chantler 1995).

## 3. Towards a critical test of available atomic physics theory

In some cases the variation between theoretical predictions is a natural consequence of the failure of one approach in a particular regime; but more often the cause remains undiagnosed and still has a magnitude of up to 10%. Hence we cannot use theory as a reliable benchmark, but conversely we can use highly accurate experiments (if they existed) as a benchmark for investigating fundamental issues in theory.

Returning to high precision experiments over the last decade claiming 1% precision or better, we find that some major limitations in technique have been avoided but that discrepancies remain (Wang *et al.* 1992; Gerward 1989; Creagh and McAuley 1995; Kiran Kumar *et al.* 1996) [Fig. 1].

This is a better situation than a relatively uncritical compilation, as for silver [Fig. 2]. However, there are several criteria for concern. In general compilations of experimental results are as follows:

(1) At least 25% may have had contamination from higher harmonics (Creagh and Hubbell 1987). The presence of harmonic contamination is not in itself a cause for inaccuracy, but requires careful control and accurate measurement of the harmonic contribution, following the principle of Barnea and Mohyla (1974). The correct treatment is analogous to that for separating contributions to intensity in lifetime measurements using beam-foil spectroscopy (e.g. Corney 1986). If uncorrected, this will lead to a systematic underestimate of the attenuation coefficient.
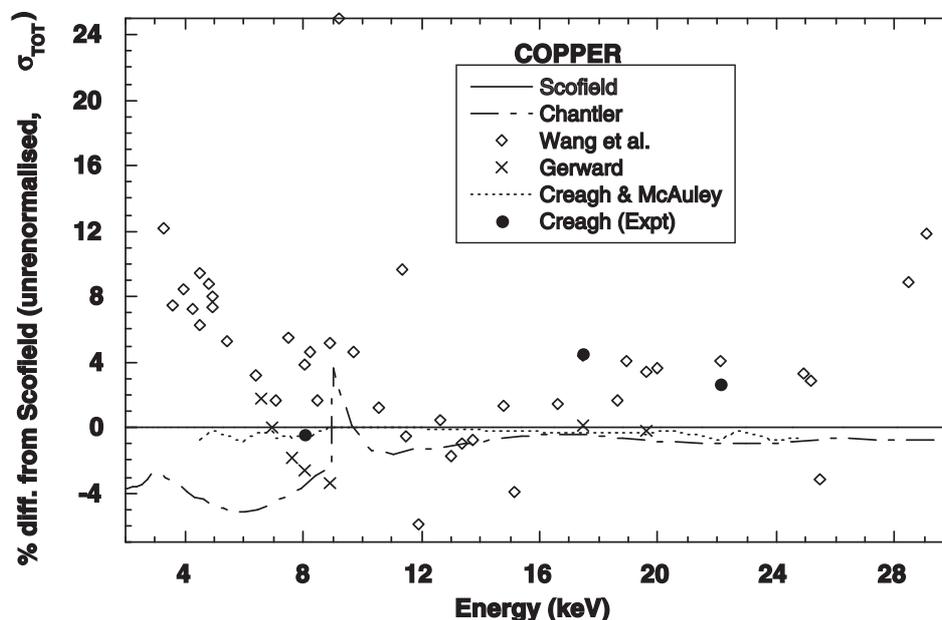
Fig. 1. Major discrepancies in the total attenuation cross-section of copper. Scattering is minor. Theory (Saloman *et al.* 1988; Chantler 1995; Creagh and McAuley 1995) and experimental (Wang *et al.* 1992; Gerward 1989; Greagh and McAuley 1995) uncertainty given by symbol size. Measurements of $f''$ or $\sigma_{pe}$ for copper have quoted 1% accuracy, but discrepancies reach 25% near the edges and 8% away from the edges. This has been stressed recently (Wang *et al.* 1992; Kiran Kumar *et al.* 1996). Theories disagree by 6%, and experiment and theory disagree by 12% away from the edges.

(2) 33% made no correction for dead time. Low fluxes through a Si(Li) detector will be hardly affected by this; but a normalisation based on a high flux measurement would be compromised. All detector types are significantly affected by this, but to a lesser extent than Si(Li) detection (e.g. Chipman 1969). Demonstrating the linearity of detection across the whole range of signals and energy is critical to accurate measurements. If uncorrected, this would tend to underestimate the attenuation coefficient.

(3) 33% used configurations with large divergence. A degree of divergence is minor if the sample alignment is accurate. However, uncollimated irradiation of 10 mm × 10 mm areas can generate 10° divergence, with consequent thickness variation of the order of 2%. Misalignment can then add several percent to the error of the result. Methods of measuring coefficients over wider energy ranges by rotating samples were observed to yield results lower by 3%. For a low divergence arrangement this should not occur, but for a modest but uncalibrated divergence this error could easily follow unless the *effective* attenuation coefficient was explicitly evaluated. If uncorrected, this would overestimate the attenuation coefficient.

Few experiments claim to approach 1% precision (Creagh and Hubbell 1995). The most reliable results quoted in the literature relate to the work of
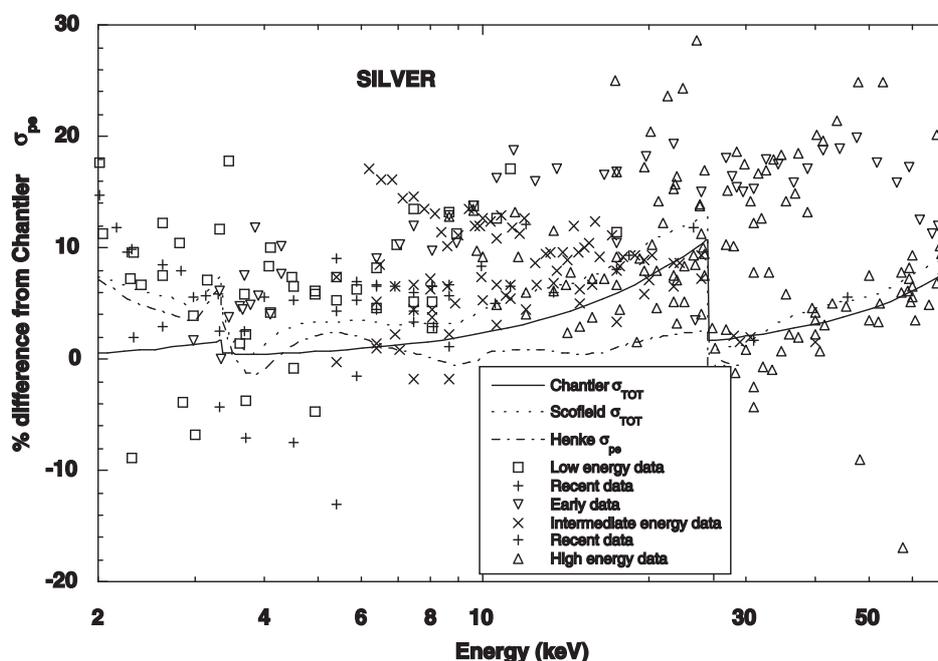
Fig. 2. Attenuation cross-sections in silver, relative to Chantler (1995) $\sigma_{pe}$. Scattering indicated by Chantler $\sigma_{TOT}$. Silver shows an array of data (Saloman *et al.* 1988) quoted at 3% but with variation of 28% or 16% for more recent measurements. Theory shows variations of 7%. Accurate 1% measurements would be extremely valuable.

Creagh *et al.* which addressed carbon, silicon and copper, and to the previous work of Gerward and Kerr Del Grande (Saloman *et al.* 1988; Gerward 1993; Creagh and Hubbell 1987, 1990). In this and similar works, these three issues have been addressed correctly, without eliminating the observed variation.

## 4. Additional criteria

(4) For single crystals or oriented samples, Laue–Bragg reflections should be avoided by rotation about the azimuthal angle and by collimation before the sample. This can yield errors of 1% or much more if not addressed. In general the nature of the sample should be evaluated carefully before the experiment (Creagh and Hubbell 1987).

(5) The Nordfors criterion relates to an optimum attenuation ratio for accurate measurement (Nordfors 1960). A plateau exists under certain conditions when $2 < \ln(I/I_0) < 4$ is satisfied. However, this criterion depends critically upon detector linearity, flux and other sources of noise, and so is not quite so clear as has been stated.

High precision measurements have used ln ratios of the order of 0.2 (Mika *et al.* 1985), which yields a statistical error, a factor of 5 worse than ideal. This criterion, like most of the others, depends on the duration of the experiment and can be overcome by collecting 25× the original photon count. Where the detectors are not photon counters (e.g. for ion chambers where the output is a voltage or current), the interpretation of final statistical precision is a major issue. For example, there have been no studies of effective statistics for ion chambers when applied to measurements of attenuation coefficients.

(6) The interpretation of the scattering contribution is related to these two issues. Conventionally, even in the best experiments, an assumption is made that either (a) the observed attenuation is the sum of photoelectric absorption, Compton scattering and Rayleigh scattering (the isolated atom approximation for coherent, elastic scattering) or (b) that the attenuation is the sum of photoelectric absorption, Compton scattering and Thermal Diffuse scattering (the bulk coherent scattering contribution away from Laue–Bragg peaks). These estimates may differ by 1% or 20% depending on Z and the photon energy. A vapour of rubidium should follow the first estimate, for example; while a perfect oriented single crystal of Rubidium could follow the second estimate. Hence the structure and orientation of the sample should be characterised to approach the required accuracy.

(7) For poor samples, small angle scattering can originate from the void structure in addition to elemental diffraction. In such cases, this should be characterised using downstream collimation or measurement of scattering distributions. Impurities from trace elements can also prevent a high precision measurement.

We have almost reached a null set of experimental data which explicitly address all these issues. Additionally:

(8) Many results have not characterised the thickness of their samples to the necessary final accuracy.

(9) Many results have not characterised their statistical precision accurately.

(10) The monochromation is often inadequate to resolve significant structure, and the average attenuation over a broad energy bandwidth is not the attenuation of the energy at the peak intensity.

This turns a naïvely simple experiment into a complex precision measurement. But it therefore yields something qualitatively new – a critical test of available atomic physics theory.


## 5. Selected best comparisons so far

A brief assessment of some of the best work to date is valuable, as it can give hints as to the optimum theory in a restricted subset of regions.

Gold, for example, gives an interesting and different structural profile for two experimental sets, and two different profiles for two theories (Fig. 3, (Kerr Del Grande 1986; Henke *et al.* 1993)). At low and medium energies, the 8% discrepancies are much larger than the claimed experimental precision of 2% and the theoretical expectation over most of this range of the order of 1%.

Chantler has addressed inconsistencies in previous theoretical approaches and produced a uniform and comprehensive result (Chantler 1994). In optimum experiments (Figs. 4 and 5 for helium and uranium, cf (Azuma *et al.* 1995; Cromer and Liberman 1981), this approach appears consistent with the current best data, yet conclusions are limited because the data do not isolate scattering contributions. Hence the most direct approach to these problems is to pursue accurate experimental investigations.

The result for helium questions the appropriate scattering computation for a given sample. Chantler has provided values for Rayleigh scattering following a simple approximation (Veigele 1973), while Saloman *et al.* (1988) use a more sophisticated Rayleigh scattering estimate based on different wavefunctions. Chantler's photoabsorption values are in agreement with the
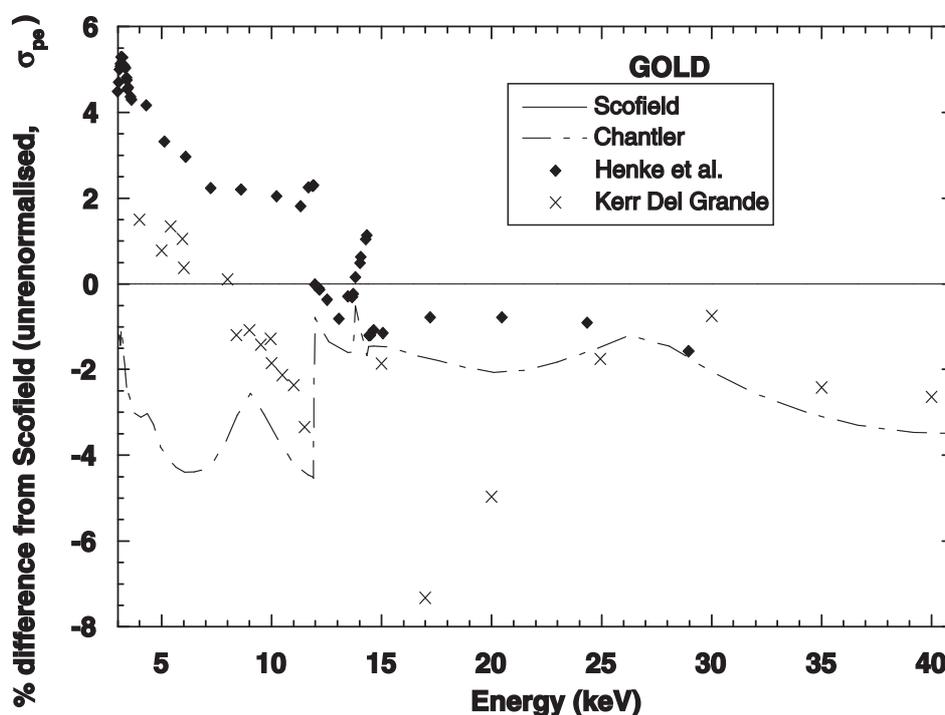


Fig. 3. Major discrepancies in the photoelectric attenuation coefficient in gold. Experimental data from Kerr Del Grande (X) (1986) with estimated uncertainty of 2%. Result of Henke *et al.* (1993) is compared.
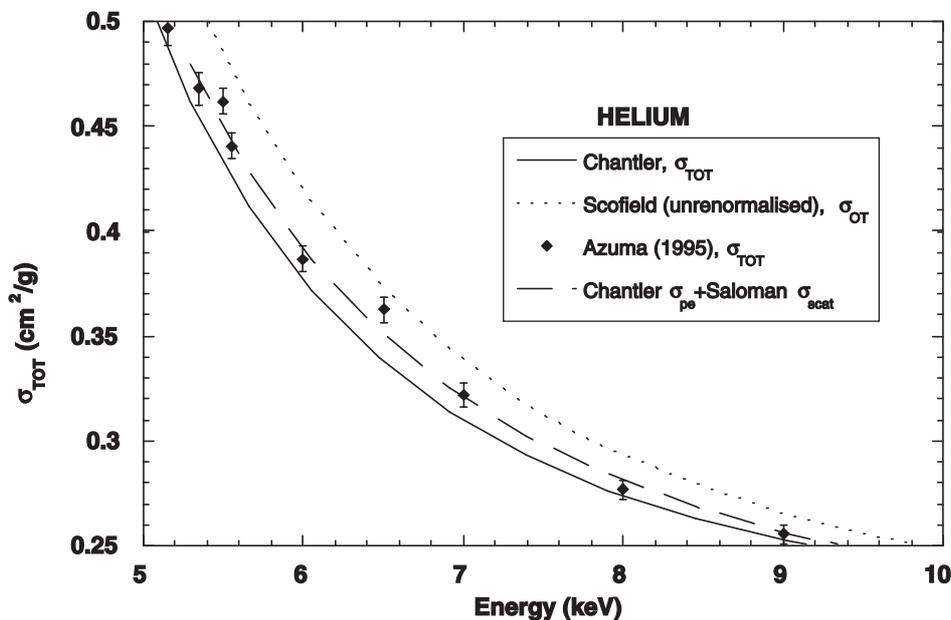
Fig. 4. Attenuation in He. Experimental data from Azuma *et al.* (1995). Chantler (1993) (line and dash) agrees with experiment, as compared to Scofield unrenormalised (1988) (dot) or renormalised. Uncertainty in scattering (which dominates above 11 keV) is indicated by variation between line and dash.

experimental results of Azuma when the scattering values of (Saloman *et al.* 1988) are used. This highlights the differences amongst Rayleigh scattering estimates. A Rayleigh cross-section is appropriate for a monatomic gas; yet the difference between the two results is a 3% discrepancy, or 10% of the scattering contribution (approximately the uncertainty of the simpler approach).

Many additional details of the region of validity of theory are given elsewhere (Chantler 1994). Here we show that precision measurement is clearly able to probe theoretical details if a precision of 0.5% or so is reliably obtained.

## 6. Current directions

Our experimental approach is quite different from the earlier work. We propose complementary measurements with the rotating anode in the School of Physics and at synchrotron facilities. A key issue is that complementary error sources will be isolated. Harmonic contamination and energy measurement are critical issues at synchrotrons, where limited time and high energy Bremsstrahlung are intrinsic to any experiment. Selected measure-
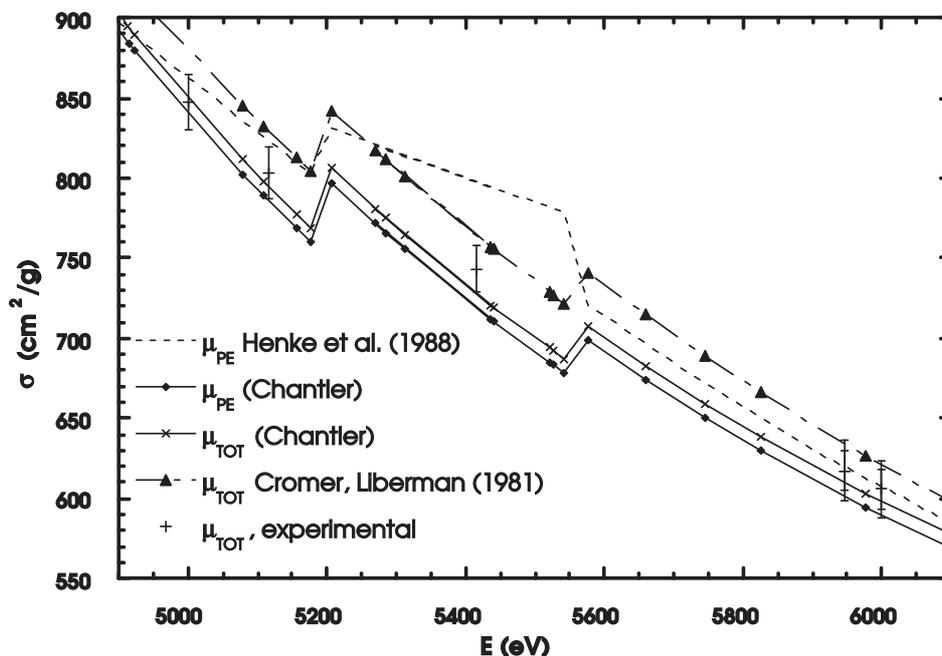
Fig. 5. Attenuation in U. Data from Kerr Del Grande (1986). Chantler (1993) agrees with experiment as opposed to Henke (dash) (1993) and Cromer-Liberman (dot-dash) (1981). Scattering is given by $\mu_{TOT} - \mu_{pe}$.

ments at local facilities can avoid these problems and address others in a time-consuming but explicit manner. Achievement of consistent results where error sources vary widely is a key signature for accuracy.

Harmonic contamination and measurement linearity will be determined *in situ* with multiple samples for a given energy, and energies will be calibrated to about an eV or 30 ppm. Local structure will therefore enhance the measurement calibration. Fig. 6 shows an example of the result of optimising the log ratio over a large range of energies, and an implementation of this approach. This actually allows $0.4 < \ln(I/I_0) < 4$ under normal conditions, as opposed to the Nordfors criterion discussed above. Characterisation of important and interesting samples of Si, Cu, Ag and Au has proceeded to the point of initial experiments at the required precision. The research is continuing.

## 7. Conclusions

We have identified major variation in the current theoretical databases, and concluded that the underlying assumptions and discrepancies can only be
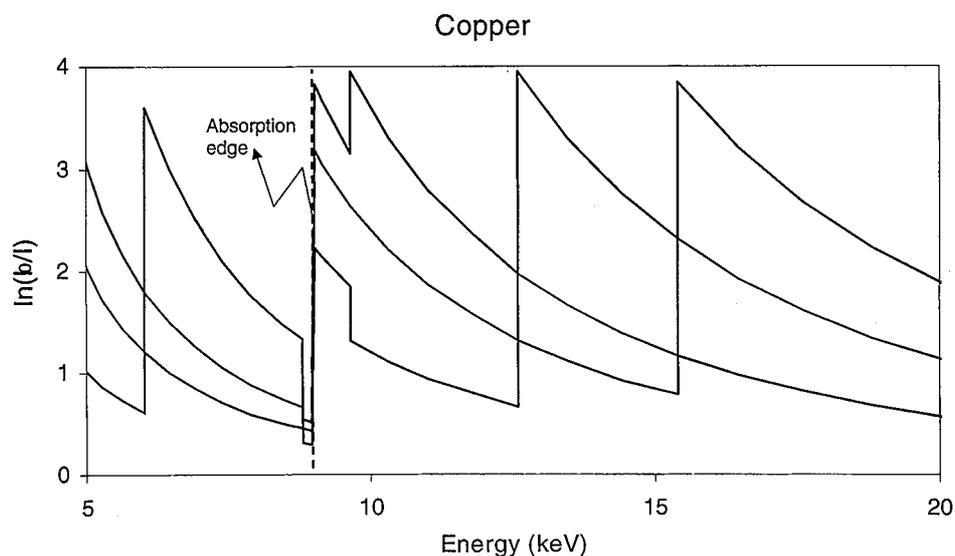
## Copper



Fig. 6. Demonstration of the optimised selection of copper target thicknesses to cover a large energy range with uniform and optimum ln $(I_0/I)$ ratios. Note that the edges are particularly crucial and that use of three thicknesses covering the full statistical plateau addresses several error sources including harmonic contamination and impurities.

addressed by direct experimental comparison. We have considered the available extensive experimental data, and find that with few exceptions, most are quite inadequate to address current theoretical dilemmas. Hence new experimental methods are actually required. Our purpose is then to point forward and commend future investigators to address all of the issues raised, which should then yield a new consistency between measurements. Our proposed experimental approach is quite different from the earlier work, and may yield an increase in precision and accuracy by an order of magnitude.

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