Experimental and theoretical determination of the L-fluorescence yields of bismuth

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Abstract
The knowledge of atomic fundamental parameters such as the mass attenuation coefficients or fluorescence yields with low uncertainties, is of decisive importance in elemental quantification involving x-ray fluorescence analysis techniques. For example, several databases giving 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. Some review articles present compilations of measured fluorescence yields values found in the literature. However reliable measurements are not so many illustrating the inherent difficulties. Mass attenuation coefficients of bismuth were determined experimentally in the photon energy range from 100 eV to 30 keV by using monochromatized synchrotron radiation at SOLEIL (France). The fluorescence yields of the three L-subshells of bismuth were also determined using a reflection geometry setup. The application of high-accuracy experimental techniques resulted in low uncertainty mass attenuation coefficients and L-subshell fluorescence yields that are directly compared to existing databases and with updated relativistic configuration mixing Dirac–Fock calculations including QED corrections.

Keywords: mass attenuation coefficients, fluorescence yields, bismuth

(Some figures may appear in colour only in the online journal)
1. Introduction

A reliable knowledge with low uncertainties of x-ray atomic fundamental parameters such as the mass attenuation coefficients and the fluorescence yields is essential in several technical fields using x-ray properties of atoms. Indeed, elemental quantification involving x-ray fluorescence analysis techniques rely on databases of mass attenuation coefficients, fluorescence yields and Coster–Kronig factors, line intensities, etc. For example, several databases giving the mass attenuation coefficients are accessible and frequently used within a large community of users [1–4]. 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 \( (E > 20 \text{ keV}) \). However, they significantly differ for low photon energies and around the absorption edges for most elements. The lower the energies, the more difficult the transmittance measurements are which led a poor number of values to be published in the literature. This explains why compilations or theoretical calculations rarely matches under 1 keV. Concerning the L-fluorescence yields, some review articles presented compilations of measured fluorescence yield values found in the literature [5, 6] and made a critical analysis in order to propose recommended values. However, from this work it is still obvious that uncertainties are quite large and in addition values for several atomic numbers are extrapolated from the fit to other existing data, illustrating the inherent difficulties.

The Laboratoire National Henri Becquerel (LNHB), the French national 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. Several studies were already published in the field [7–9], and in the present paper we focussed on bismuth, a high-Z element. In a recent article, we already determined the L-fluorescence yields of bismuth [10] using a radioactive source of \(^{210}\text{Pb}\) to get absolute values of intensities as we could measure the activity of the source. We also relied on mass attenuation coefficients taken from the literature. In the present work, we propose a new methodology to experimentally obtain a consistent set of fundamental parameters. As a first step we measured the transmission of several Bi foils in order to derive the mass attenuation coefficients over a large photon energy range, from 100 eV up to 30 keV, using monochromatized synchrotron radiation as well as an in-lab tunable and monochromatic x-ray source [7]. Smaller energy steps were made around the \( L \) and \( M \) absorption edges in order to describe the absorption fine structures if any. The second step aimed at determining the partial \( L \) photoelectric cross sections as well as the fluorescence yields by a methodology using a minimum of hypotheses and pre-requisites. These parameters are derived from fluorescence spectra acquired by photoionization of selective vacancies in the subshells.

2. Theory

The photoionization cross-sections, radiative and radiationless transition rates were calculated using the MCDFGME code of Desclaux and Indelicato [11–13]. The wavefunctions were obtained using the single-configuration approach, with magnetic (Gaunt) and first order retardation terms of the Breit interaction included in the self-consistent variational method. The one-electron self-energy was computed from the values of Mohr and Kim [14], and the self-energy screening was obtained using the Welton method developed by Indelicato and Desclaux [12]. To compute the vacuum polarization contributions we used the following approach: the Uehling contribution is evaluated to all orders by being included the self-consistent field, and the Wichmann–Kroll, and Kallen–Sabry contributions are included perturbatively. Higher-order Breit retardation terms and other QED corrections were added as perturbations. The continuum electron wavefunction in the final state is evaluated by solving the Dirac–Fock equations, with full exchange, and is normalized to represent one ejected electron per unit energy [15, 16].

To obtain the radiative transition rates, the so-called optimized levels method is used to calculate the wavefunctions and energies of the states. In this method, all possible transitions between states are calculated using full relaxation of both initial and final wave functions, hence providing more accurate energies. In is noted that spin–orbitals of the initial and final states are, therefore, not orthogonal since they are optimized separately. To deal with the nonorthogonality of the wavefunctions, the code uses the formalism described by Löwdin [17].

A two-step process model was used to calculate the radiationless transitions, in which the transition is treated independently from the primary ionization. In accordance to this model, the primary ejected electron in the inner-shell ionization process does not interact with the Auger electron and the interaction of the core vacancy state with the continuum electron is weak, which enables the use of the perturbation theory to calculate the radiationless transition rates. Initial state wavefunctions were generated for configurations that contain one initial inner-shell vacancy while final state wavefunctions were generated for configurations that contain two vacancies in higher subshells.

No orbital relaxation was allowed between the initial and final bound state wavefunctions during the calculation of the radiationless transition rates and photoionization cross-sections, to ensure orthogonality. However, these parameters were calculated using the correct transition energies obtained in previous independent calculations of the initial and final state wavefunctions [18].

3. Characteristics of the photon sources

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. 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 SOLEIL synchrotron, France, that includes two branches (XUV: from 100 eV to 1.8 keV and hard x-ray: from 3 keV to
35 keV). The gap between 1.8 keV and 3 keV was filled using the SOLEIL source of the laboratory [19].

3.1. The hard x-ray branch at SOLEIL Metrology beamline

The monochromator device is composed of a double Si(1 1 1) crystal whose Bragg angle is determined with a rotary position encoder that needs a calibration. The calibration of the monochromator is obtained by scanning the beam energy across the absorption edges of several metallic foils, assigning the Bragg angles corresponding to the edge energies reported by Deslattes [20] to the first derivatives of the measured angular absorption spectra. The comparison with the absolute angles gives an offset that is set to the monochromator device. The residual difference between the angular positions given by the encoder and the values derived from the tabulated absorption edges is presented in [9] and is kept below 0.04%. The energy selection and the minimization of harmonics or stray light were realized as discussed in [9], and so we estimated the uncertainty budget in the same manner.

The transmission measurements are performed using a beam collimated at $3 \times 3 \text{ mm}^2$ or $3.5 \times 3.5 \text{ mm}^2$, assuming thus these areas to be representative of the average thickness of the whole target. Once the energy calibration is achieved, long scanning sequences with 10, 25 and 50 eV steps are carried out within the whole available photon energy range, closer steps of 5 eV around the $K$ absorption edge and 1 and 2 eV in the vicinity of $L$ absorption edges being employed. The transmitted photon intensities are recorded by means of an AXUV-Al photodiode whose dark noise is subtracted to all current values to derive an unbiased transmittance.

3.2. The laboratory source SOLEX

The laboratory source of low energies x-rays (SOLEX) has been already used in recent works to derive the mass attenuation coefficients of several materials [7]. This x-ray source consists of an x-ray tube and one bent crystal as monochromator, the photon energy calibration following the same procedure as detailed in the cited paper. Several crystals are available to cover the different photon energy ranges defined by the maximum and minimum Bragg angles of the setup. 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 us to use an energy-dispersive detector. This cancels the stray light and monochromaticity issues. Specific issues concerning the detector linearity or dead-time correction are taken into account as described in [21].

The photon energy range covered here starts at 1.1 keV and goes up to 4.3 keV in order to obtain a large overlap with previous values obtained at the hard x-ray branch. Since the mass and area of the employed sample cannot be characterized in an independent manner (thin sample), a fit of the measured transmittance is done in the overlapping energy range to derive a mass per unit area (assuming a homogeneous density of bulk tin) by adjusting it with the absolute mass attenuation coefficients values obtained at the hard x-ray branch.

3.3. The XUV branch at SOLEIL metrology beamline

The XUV branch is equipped with several focusing mirrors, a variable line-spacing (VLS) grating for the photon energy selection, filters and an order-sorter for minimizing the harmonics. Three VLS gratings are available adapted to three different energy ranges: 75, 300 and 1200 lines mm$^{-1}$. The energy range of the branch used for this experimental work starts at 100 eV and goes up to 1.8 keV. By combining the use of filters and of the three mirrors order-sorters which have several available coatings, this energy range is sliced in parts. The different combination of gratings, filters and order-sorter are used in such a way that the harmonics are kept under 1% anytime. The transmission measurement method is different from the other presented techniques because the spot size provided by the branch is 100 µm high and 200 µm wide (FWHM values), which means that the average mass per unit area is not a relevant parameter anymore if the sample roughness is large with a typical spatial length of the same order of magnitude.

4. Determination of the mass attenuation coefficients

The mass attenuation coefficient, $(\mu/\rho)$, is the parameter standing for the interaction probability of a photon beam in matter. 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:

$$\left(\frac{\mu}{\rho}\right) = -\frac{1}{\rho \cdot x} \ln \left(\frac{I}{I_0}\right)$$  

where $I$ and $I_0$ are the transmitted and incident photon intensities respectively, $\rho$ (in g cm$^{-3}$) and $x$ (in cm) are respectively the target density and thickness, $(\mu/\rho)$ is the energy-dependent mass attenuation coefficient in cm$^2$ g$^{-1}$. A transmission measurement procedure is a convenient way to determine the mass attenuation coefficients, using a monochromatic photon beam of low divergence. Consequently, the final uncertainty budget is linked to the target characteristics and the photon flux intensities. In order to achieve the best possible uncertainty budget associated with the counting statistics, samples must have a thickness which satisfies: $2 \leq \ln (I_0/I) \leq 4$ according to Nordfors et al [22] criterion.

4.1. Bismuth samples characteristics

Accurate values of the sample characteristics are also required to derive absolute values of the atomic parameters. Bismuth was studied in the form of metal foils. A thick metal foil was acquired from Goodfellow corporation [23] which were chosen with a mass purity better than 99.97% and two other self-supported thin foils were prepared by sputtering techniques. Measuring absolute mass attenuation coefficients


| N° | Thickness* (µm) | Mass (g) | Area (cm²) | Mass/Area (g·cm⁻²) | Purity (%) |
|----|-----------------|----------|------------|---------------------|-----------|
| 1  | 15              | 1.1973(9) × 10⁻² | 8.55(5) × 10⁻¹ |                         | 99.97     |
| 2  | 0.8             | 1.126(4) × 10⁻³  |             | 1.44(1) × 10⁻⁴      | 99.9      |
| 3  | 0.2             | 1.44(1) × 10⁻⁴  |             |                     | 99.9      |

*The thicknesses are nominal and only mass per area are relevant for the experimental determination.

Table 2. Uncertainty budget: relative standard uncertainty of each contributor.

| Contribution | sample 1 (%) | sample 2 (%) | sample 3 (%) |
|--------------|--------------|--------------|--------------|
| Mass         | 0.078        | 0.4          | 0.6          |
| Area         | 0.061        |              |              |
| Target purity| 0.02         | 0.2          | 0.2          |
| Transmission | 0.6          | 0.36         | 0.1          |

requires the knowledge of the number of atoms interacting with the photon beam. To derive absolute values for the mass attenuation coefficients from equation (1), density and thickness must be known with the smallest possible uncertainty. It appeared to be difficult to measure a thickness in the range of micrometres or less with accurate techniques other than x-ray transmission measurements, which relies on mass attenuation coefficients. Measuring the mass and area of the samples has the advantage of being more accurate and independent from x-ray analysis techniques. The mass is determined by weighting 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. It allows for several magnifications in order to provide an adequate enlargement necessary to follow a complicated shape with accuracy. The remaining sources of inaccuracy are the roughness and thickness homogeneity of the samples that have to be evaluated.

Three samples of different thicknesses were chosen in order to have measurable transmission fluxes in the energy range from 0.1 keV up to 35 keV. The table 1 presents the characteristics of the samples used in the different experiments. The table 2 gives the different contributions to the uncertainty budget of the mass attenuation coefficient measurements. Samples 2 and 3 are very thin free-standing foils. Unfortunately, due to their preparation technique, no independent measurement of mass and area are possible as they are too fragile for any handling. Therefore, the average mass per unit area was estimated by fitting the transmittance measurement in an overlapping energy range with the thickest foil. The transmittance of sample 2 was scaled to the absolute values determined by sample 1 between 3 and 10 keV and the transmittance of sample 3 was scaled between 0.8 and 1.8 keV with that of sample 2.

4.2. Experimental results and uncertainty budget

The sample preparation technique could also add an important bias on the density value from bulk: laminated foils or deposited materials with any technique could end up with several percent deviation from tabulated bulk density. The purity of the sample can be accounted for by including a correction factor \( k_P \) [9] in equation (1):

\[
\left( \frac{\mu}{\rho} \right) = - \frac{1}{\rho \times x} \ln \left( \frac{I}{I_0} \right) \times k_P = - \frac{A}{M} \times \ln (T) \times k_P
\]

where \( M \) is the mass of the sample in g, \( A \) its area in cm², \( T \) is the transmission ratio and \( k_P = 1 \) is used in the error calculations to take into consideration the additional uncertainty due to the purity of the samples.

To evaluate the uncertainty of the experimental mass attenuation coefficients, equation (2) was derived according to all the influence quantities as mentioned in the ‘Guide to the expression of uncertainty in measurement’ [24]. The uncertainty budget was evaluated using the following formula:

\[
\left( \frac{u}{\mu} \right)^2 = \left( \frac{u(M)}{M} \right)^2 + \left( \frac{u(A)}{A} \right)^2 + \left( \frac{u(T)}{T} \right)^2 + \left( \frac{u(k_P)}{k_P} \right)^2
\]

The x-ray transmission measurement, using the procedures described in detail in [7], is a sequential method as it requires to remove the sample from the beam in order to measure the incoming beam \( I_0 \). The measurements resulted in a set of transmission data in the photon energy range from 100 eV to 35 keV (figure 1 left), from which the energy dependent mass attenuation coefficient was calculated, covering L-, M, and N-absorption edges of Bi.

These results are compared to theoretical and experimental values compiled in other published articles or databases such as [1, 4, 25–27]. The relative differences between the new measurements and other tabulated values are presented in figure 1 right. This graph plots the deviation in percent defined as follows:

\[
\frac{\Delta \mu}{\mu} = \frac{\mu_{EXP} - \mu_{DB}}{\mu_{DB}} \times 100
\]

where \( \mu_{EXP} \) stands for the presently measured mass attenuation coefficients and \( \mu_{DB} \) stands for values from a published database. Different behaviours can be observed. Between Bi M₁ and L₃ absorption edges, the relative differences are 2 or 3 percents. Below the M₃ absorption edge, the discrepancies with Henke table [1] are higher than with other databases. For photon energies below 500 eV, the databases are discrepant between themselves and the experimental values are closer to the Henke values.
5. X-ray fluorescence measurements

5.1. Determination of the relative L partial fluorescence yields

5.1.1. Equation of the emitted fluorescence. The x-ray fluorescence of a sample is traditionally studied using an experimental setup such as presented in figure 2. The emitted x-ray fluorescence following the photoionization is the result of several processes that include the attenuation of the incoming and emitted photons in the target, the photoelectric effect and atomic relaxation including subshell rearrangements.

The general formula linking the number of counts in the full-energy peak due to a specific x-ray line to the intensity of the incoming photons beam is:

$$ I_i \eta = \int_0^1 I_0 \Omega \omega_i \tau_{i,0} \frac{M}{A} \times \exp \left( -\mu_0 \frac{M}{A} \times \frac{x}{\sin(\beta)} \right) \times \exp \left( -\mu_i \frac{M}{A} \times \frac{x}{\sin(\theta)} \right) \times \frac{dx}{\sin(\beta)} $$

(5)

where $I_0$ is the number of photons per second of the incoming beam with energy $E_0$ and $I_i$ is the area of the full-energy peak for characteristic x-rays with energy $E_i$, $\eta_i$ is the detection efficiency at photon energy $E_i$, $\Omega$ the solid angle of detection, $\omega_i$ the partial fluorescence yield of the diagram line of interest, $\tau_{i,0}$ the partial photoelectric coefficient of shell $i$ at photon energy $E_0$, $M$ and $A$ are the mass in g and area in cm$^2$ of the sample, $\beta$ is the incidence angle and $\theta$ the detection angle (figure 2). $\mu_0$ and $\mu_i$ are the total mass attenuation coefficients at the excitation energy $E_0$ and at the characteristic energy $E_i$, respectively.

5.1.2. Experimental conditions. The fluorescence experiment was conducted at the hard x-ray branch of the Metrology beamline at SOLEIL, using a reflection geometry (figure 2). The Bi sample was installed at 45° with respect to both the excitation photon beam and the energy-dispersive spectrometer, thus one can write $\beta = \theta = \frac{\pi}{4}$. The energy-dispersive detector was a 17 mm$^2$-area FastSDD from Amptek. An AXUV100G photodiode from International Radiation Detectors, Inc. was used to monitor the incoming photon flux. Before, its efficiency was absolutely calibrated with a cryogenic radiometer in the photon energy range from 3 keV to 30 keV [28]. This diode was placed in the path of the beam, behind the sample to collect the beam transmitted through this one. The incident photon flux, $I_0$, was derived from the photodiode calibration and from the transmission measurements performed in the first part of the study. In total, thirty spectra were collected at photon energies starting just above the $L_3$ absorption edge up to 20 keV with selected energies between the absorption edges. The duration of the acquisition was chosen in order to record more than $10^5$ events in the full-energy peak corresponding to the most intense diagram line of each subshell. In every spectrum, the $\alpha_{1,2}$ line was found to have more than $2 \times 10^5$ counts, the $\beta_1$ line has more than $1.5 \times 10^5$ counts and the $\beta_3$ line more than $4 \times 10^5$ counts, thus reducing the relative uncertainty due to counting statistics to 0.22%, 0.26% and 0.5%, respectively.

5.1.3. Spectra processing. The electronic configuration of bismuth is $[Xe]4f^{14}5d^{10}6s^26p^3$. The subshells $N_1$ to $N_7$, $O_1$ to $O_5$ and $P_1$ and $P_2$ are filled with electrons, thus available...
for x-ray transitions. The most important transitions are presented in table 3. The spectra (some examples are proposed in figure 3) were processed using the COLEGRAM software [29]. X-ray peaks were fitted using Voigt profiles and the Lorentzian width was fixed for each line by adding the widths of the two levels of the transition to take the natural x-ray linewidths into account, as presented in table 3. The detector absolute efficiency was measured for several points as in [21] and a fitting curve using the deduced detector geometrical characteristics (thickness of the crystal and dead layers) was used to derive its absolute efficiency. This one was found to vary between 0.6 and 0.95 in the energy range of interest.

With incoming photon energy $E_0$ between the $L_1$ and $L_2$ absorption edges, only diagram lines with initial level $L_3$ appear and no contribution from transfer of initial vacancies in higher subshell is allowed. The $\alpha_1$ and $\alpha_2$ lines are not resolved by the detector and they are taken as a single line at photon energy 10 800 eV. The lines $\beta_2$ and $\beta_{15}$ are not distinguishable either at 12 970 eV, the other contributions are the $l$, $s$, $t$, $u$ and $\beta_6$ that are listed in table 4. With incoming photon energy $E_0$ between the $L_2$ and $L_1$ absorption edges, the diagram lines with initial level $L_2$ are obtained, i.e. $\beta_1$, $\eta$, $\gamma_1$, $\gamma_5$, $\gamma_6$, $\gamma_7$ and $\nu$. They are present in the spectrum together with the previous ones. The intensity of the former lines are now affected by the Coster–Kronig factor $f_{23}$. Another issue appeared with the diagram line $\beta_{2,15}$ which is now hidden by $\beta_1$. To avoid a bias in the measurement of the $\beta_1$ line area, the contribution of the area of $\beta_{2,15}$ was fixed to its average ratio value with respect to $\alpha_{1,2}$. Moreover, the lines $\gamma_6$, $\gamma_7$ and $\nu$ are not separated by the detector and are fitted together. For excitation photon energies above the $L_1$ absorption edge, the diagram lines with initial level $L_1$ are obtained, i.e. $\beta_3$, $\beta_4$, $\beta_9$, $\beta_{10}$, $\gamma_4$ and $\gamma_{14}$, $L_1 - P_{2,3}$ and $\gamma_{2,3}$. The detector being unable to separate $\gamma_{2,3}$ from $\gamma_{6,8}$ and $\nu$, they are fitted as a single gaussian line, the area of which is then divided in two parts: the first one being the average ratio of $\gamma_{6,8}$ and $\nu$ with respect to $\gamma_1$, the rest being the contribution of $\gamma_{2,3}$.

### Table 3. Main characteristics of Bi diagram lines (energies from Deslattes [20] except $^a$ that are determined from [20, 30], widths from Campbell & Papp [31, 32]).

| Diagram line | Energy / eV | Natural width / eV |
|--------------|-------------|--------------------|
| $l (L_3 - M_3)$ | 9420.4 | 21.47 |
| $t (L_3 - M_2)$ | 9725.6 | 10.07 |
| $s (L_3 - M_1)$ | 10 242.2 | 14.87 |
| $\alpha_{1,2} (L_3 - M_{1,2})$ | 10 830 | 8.85 |
| $\beta_6 (L_3 - N_1)$ | 12 481.7 | 15.87 |
| $\beta_{15} (L_3 - N_{1,2})$ | 12 955 | 10.07 |
| $u (L_3 - N_{0,2})$ | 13 259.4 | 6.49 |
| $\beta_3 (L_3 - O_1)$ | 13 268.3$^a$ | >6.27 |
| $\beta_3 (L_3 - O_{1,5})$ | 13 402$^a$ | >6.27 |
| $\eta (L_2 - M_1)$ | 11 712 | 21.42 |
| $\beta_1 (L_2 - M_1)$ | 13 024 | 8.8 |
| $\gamma_5 (L_2 - N_1)$ | 14 733 | 15.82 |
| $\gamma_1 (L_2 - N_3)$ | 15 248 | 10.02 |
| $\nu (L_2 - N_{0,2})$ | 15 552 | 6.42 |
| $\gamma_6 (L_2 - O_1)$ | 15 560.3$^a$ | >6.22 |
| $\gamma_6 (L_2 - O_{1,5})$ | 15 693.1$^a$ | >6.22 |
| $\beta_4 (L_2 - M_1)$ | 12 691 | 23 |
| $\beta_1 (L_1 - M_1)$ | 13 211 | 20.9 |
| $\beta_{10} (L_1 - M_3)$ | 13 698.87 | 14.88 |
| $\beta_9 (L_1 - M_5)$ | 13 806.82 | 14.88 |
| $\gamma_{2,3} (L_1 - N_{2,3})$ | 15 650 | 19 |
| $\gamma_{2,3} (L_1 - O_1)$ | 16 278.6$^a$ | >12.3 |
| $\gamma_{2,3} (L_1 - O_{1,5})$ | 16 302.4$^a$ | >12.3 |
| $\gamma_{2,3} (L_1 - P_{2,3})$ | 16 380$^a$ | >12.3 |

5.1.4. Experimental results: the partial fluorescence production cross sections. Using equation (5) as ratios from diagram lines of the same L subshell allows to become independent from the solid angle of detection, the incoming intensity and the photoelectric cross sections. The results of the relative emission rates are normalized to the most intense diagram line of each subshell and presented in table 4 with their associated uncertainties.

5.2. Determination of the photoelectric cross sections

Partial photoelectric cross-sections can be chosen in the literature as for example from EPDL97. In this case, the values may not be compatible with the absolute mass attenuation coefficients measured in the first part. Indeed, significant differences arose between our experimental values and the mass attenuation coefficients proposed by the EPDL97 table as presented as solid lines on figure 4. Discrepancies are visible close to the edges and at larger energies. Using these values would lead to a biased estimate of the fluorescence yield and probably an unreliable estimate of the Coster–Kronig factors. Another possibility is to extrapolate the mass attenuation coefficients from their values between two L edges to higher photon energies, through transition edges energies to estimate the partial photoelectric cross sections at energies where they cannot be directly measured. This method is presented as dashed lines on figure 4. The result is not satisfactory either as the tendency for $\gamma_2$ and $\gamma_3$ is not physical. We used a different approach: we used the mass attenuation coefficients for energies lower than the next absorption edge and then we hooked up the tendency curves given by EPDL97 in order to get the same profiles for $\tau$. For example, $\gamma_3$ is chosen equal to $\mu - \mu_M$ ($\mu_M$ is the fitting curve of the measured mass attenuation coefficients for photon energies below the $L_3$ edge) for energies lower than $E_{L_3}$ and is proportional to EPDL97 values for energies larger than $E_{L_3}$. The same method is applied for $\gamma_2$ and then $\gamma_1$ is calculated as the difference between $\mu$ and $\mu_M$, $\gamma_3$, and $\gamma_2$. The resulting partial cross sections are presented in figure 4 as dotted line.

5.3. Evaluation of partial $L$-fluorescence yields

The fluorescence production cross sections of diagram lines belonging to the same subshell are summed in order to provide better accuracy of the partial fluorescence yields by improving the overall counting statistics. Most of parameters of equation (5) are independently known, except the partial fluorescence yields $\omega_i$. The integration of equation (5) gives the fluorescence production cross section $\sigma_i$: 

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Figure 3. Spectra acquired at incident photon energies of 13.6, 16.2 and 17 keV respectively. The results of the fitting analysis are presented as red lines for individual peaks and blue for the resulting global fit.

Table 4. Comparison of the relative intensities of the Bi diagram lines with data from the literature.

| Diagram line | Relative intensities (this work) | Salem (1971–72) [33, 34] | McCrary (1972) [35] | Scofield (1974) [36] |
|--------------|----------------------------------|---------------------------|----------------------|----------------------|
| $l (L_3 - M_1)$ | 0.0589(10)                      | 0.0436                    | 0.056(2)             | 0.0532               |
| $t (L_3 - M_2)$ | 0.0005(3)                       |                           |                      | 5.95 × 10⁻⁴          |
| $s (L_3 - M_3)$ | 0.0010(1)                       |                           |                      | 5.59 × 10⁻⁴          |
| $\alpha_{1,2} (L_3 - M_{4,5})$ | 1                               | 1⁺                         |                      | 1                    |
| $\beta_6 (L_3 - N_1)$ | 0.0175(18)                      | 0.018(4)                  |                      | 0.0133               |
| $\beta_{2,3} (L_3 - N_{4,5})$ | 0.1837(13)                      | 0.205                     |                      | 0.194                |
| $u (L_3 - N_{6,7})$ | 0.0328(21)                      |                           |                      | 1.61 × 10⁻⁴          |
| $\beta_7 (L_3 - O_1)$ | 0.00237                         |                           |                      | 0.0250               |
| $\beta_8 (L_3 - O_{4,5})$ | 0.028                            |                           |                      |                      |
| $\eta (L_2 - M_1)$ | 0.0327(9)                        | 0.0214                    |                      | 0.0273               |
| $\beta_3 (L_2 - M_4)$ | 1                               | 1                         |                      | 1                    |
| $\gamma_5 (L_2 - N_1)$ | 0.0122(16)                      |                           |                      | 0.0071               |
| $\gamma_7 (L_2 - N_2)$ | 0.224(3)                        |                           |                      | 0.207                |
| $\nu (L_2 - N_{6,7})$ | 0.0398(5)                        |                           |                      | 9.1 × 10⁻⁴          |
| $\gamma_8 (L_2 - O_1)$ | 1.56 × 10⁻⁴                     |                           |                      | 0.0275               |
| $\gamma_6 (L_2 - O_2)$ | 0.082(22)                       | 0.116(15)                 |                      | 0.105                |
| $\beta_9 (L_1 - M_2)$ | 0.94(4)                          | 0.81                      | 0.88(7)              | 0.934                |
| $\beta_3 (L_1 - M_4)$ | 1                               | 1                         |                      | 1                    |
| $\beta_9 (L_1 - M_5)$ | 0.070(15)                        |                           |                      | 0.0346               |
| $\gamma_3 (L_1 - N_{2,3})$ | 0.050(10)                       |                           |                      | 0.517                |
| $\gamma_2 (L_1 - O_2)$ | 0.51(5)                          |                           |                      | 0.525                |
| $\gamma_4 (L_1 - O_{2,3})$ | 0.052(22)                       | 0.116(15)                 |                      | 0.105                |
| $(L_1 - P_{2,3})$ | 0.032(10)                        |                           |                      | 0.0046               |

* Means that the ratio was redetermined by summing $\alpha_1$ and $\alpha_2$ contributions as they are not distinguished in our work.

Figure 4. Partial photoelectric cross sections. The $\tau_{1,2,3}$ are represented in blue, red and green respectively. Solid lines represent EPDL97 values, dashed lines an extrapolation from the mass attenuation coefficients and the dotted lines represent the adopted values.
The equation (6) is valid for K-fluorescence yields but must be slightly modified for L-lines in order to take into account the Coster–Kronig effects: the shift to a higher subshell of the initial vacancy [37]. The Coster–Kronig transition probabilities are represented by the $f_{ij}$ parameters. The equation (6) is modified accordingly. Indeed, in the case of a diagram line starting from a vacancy in the $L_3$ subshell, $\tau_0$ becomes $\tau_{3,0}$ for incoming photons with an energy $E_0$ between the $L_3$ and $L_2$ absorption edges. Denoting $f_{L_3}$, the Coster–Kronig factor from subshell $k$ to subshell $l$, it changes in $\tau_{3,0} + f_{23} \times \tau_{2,0}$ and in $\tau_{3,0} + f_{23} \times \tau_{2,0} + (f_{13} + f_{12} \times f_{23}) \times \tau_{1,0}$ for excitation photons with energies $E_0$ between the $L_2$ and $L_1$ absorption edges and above the last one, respectively. In the case of a diagram line starting with a vacancy in the $L_2$ subshell, $\tau_0$ becomes $\tau_{2,0}$ and $\tau_{2,0} + f_{12} \times \tau_{1,0}$ for excitation photons with energies between the $L_2$ and $L_1$ absorption edges and above the last one, respectively. Thus, depending on which subshell the primary vacancy is created as well as the diagram line considered, the fluorescence production cross sections values $\sigma$ from equation (6) are presented in table 5.

5.3.1. Results and discussion. The results for the three partial fluorescence yields derived from the 99 spectra are presented
in figure 5. The jumps are the signature of the Coster–Kronig factors. The three partial L fluorescence yields values are presented in table 6 together with other values quoted from the literature. If a strong agreement is observed with our former values, the agreement is good but slight discrepancies are still noticeable with theoretical calculations.

6. Conclusion

A set of atomic fundamental parameters for bismuth were measured and a new methodology was proposed in order to derive partial quantities. First of all, the total mass attenuation coefficients have been determined in the photon energy range from 100 eV to 30 keV. Comparisons of the experimental values with tabulated ones show a small deviation for photon energies above 1 keV with only large discrepancies around the L absorption edges, our experimental data including the fine structures. Our experimental work is a contribution to increasing the reliability of the mass attenuation coefficients as a careful estimation of the associated uncertainties was made, as well as a contribution to reducing them as much as possible. New values of the partial L fluorescence yields were also measured and an excellent agreement was found with the MCDFGME calculations.

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References

[1] Henke B L, Gullikson E M and Davis J C 1993 X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50–30 000 eV, Z = 1–92 At. Data Nucl. Data Tables 54 181–342
[2] Elam W T, Ravel B D and Sieber J R 2002 A new atomic database for x-ray spectroscopic calculations Radiat. Phys. Chem. 63 121–8
[3] Ebel H, Svagera R, Ebel M F, Shaltout A and Hubbell J H 2003 Numerical description of photoelectric absorption coefficients for fundamental parameters programs X-Ray Spectrom. 32 442–51
[4] Berger M J, Hubbell J H, Seltzer S M, Chang J, Coursey J S, Sukumar R, Zucker D S and Olsen K 2010 XCOM: Photon Cross Section Database (version 1.5). [Online] Available: http://physics.nist.gov/xcom [2018, July 16]. (Gaithersburg, MD: National Institute of Standards and Technology)
[5] Campbell J L 2003 Fluorescence yields and Coster–Kronig probabilities for the atomic L subshells At. Data Nucl. Data Tables 85 291–315
[6] Campbell J L 2009 Fluorescence yields and Coster–Kronig probabilities for the atomic L subshells. Part II: L1 subshell revisited At. Data Nucl. Data Tables 95 115–24
[7] Ménessuen Y and Lépy M-C 2010 Mass attenuation coefficients in the range 3.8 ≤ E ≤ 11 keV. K fluorescence yield and K//K0, relative x-ray emission rate for Ti, V, Fe, Co, Ni, Cu, and Zn measured with a tunable monochromatic x-ray source Nucl. Instrum. Methods Phys. Res. B 268 2477–86
[8] Ménessuen Y and Lépy M-C 2011 Characterization of the metrology beamline at the SOLEIL synchrotron and application to the determination of mass attenuation coefficients of Ag and Sn in the range 3.5 < E < 28 keV X-Ray Spectrom. 40 411–6
[9] Ménagesuen Y, Gerlach M, Polliakowski B, Unterumsberger R, Haschke M, Beckhoff B and Lépy M-C 2016 High accuracy experimental determination of copper and zinc mass attenuation coefficients in the 100 eV to 30 keV photon energy range Metrologia 53 7–17
[10] Ménagesuen Y, Boyer B, Rodrigues M and Lépy M-C 2016 Measurement of partial L fluorescence yields of bismuth using synchrotron radiation Appl. Radiat. Isot. 109 133–8
[11] Desclaux J P 1975 A multiconfigurational relativistic Dirac–Fock program Comput. Phys. Commun. 9 31–45
[12] Indelicato P and Desclaux J P 1990 Multiconfiguration Dirac–Fock calculations of transition energies with QED corrections in three-electron ions Phys. Rev. A 42 5139
[13] Indelicato P, Gorceix O and Desclaux J P 1987 Multiconfigurational Dirac–Fock studies of two-electron ions. II. Radiative corrections and comparison with experiment J. Phys. B: At. Mol. Phys. 20 651
[14] Mohr P J and Kim Y-K 1992 Self-energy of excited states in a strong Coulomb field Phys. Rev. A 45 2277
[15] Grant I P and Quiney H M 1988 Foundations of the relativistic theory of atomic and molecular structure Adv. At. Mol. Phys. 23 37–86
[16] Indelicato P 1995 Projection operators in multiconfiguration Dirac–Fock calculations: application to the ground state of heliumlike ions Phys. Rev. A 51 1132
[17] Löwdin P-O 1955 Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin–orbitals, and convergence problems in the method of configurational interaction Phys. Rev. 97 1474–89
[18] Sampaio J M, Madeira T I, Marques J P, Parente F, Costa A M, Indelicato P, Santos J P, Lépy M-C and Ménessuen Y 2014 Approaches for theoretical and experimental determinations of K–shell decay rates and fluorescence yields in Ge Phys. Rev. A 89 012512
[19] Bonnelle C, Jonnard P, André J-M, Avila A, Laporte D, Ringueu H, Lépy M-C, Plagnard J, Ferreux L and Protas J-C 2004 SOLEX: a tunable monochromatic x-ray source in the 1–20 keV energy range for metrology Nucl. Instrum. Methods Phys. Res. A 516 594–601
[20] Deslattes R D, Kessler E G, Indelicato P, de Billy L, Lindroth E and Anton J 2003 X-ray transition energies: new approach to a comprehensive evaluation Rev. Mod. Phys. 75 35–99
[21] Ménessuen Y and Lépy M-C 2012 Efficiency calibration and surface mapping of an energy-dispersive detector with
SOLEX: a compact tunable monochromatic x-ray source

Nucl. Instrum. Methods Phys. Res. A 695 193–6

[22] Nordfors B 1960 The statistical errors in x-ray absorption measurements Arkiv Fys. 18 37–47

[23] Goodfellow Cambridge Limited (GB) Consultation date: 2017 www.goodfellow.com/

[24] JCGM 2008 Evaluation of measurement data—Guide to the expression of uncertainty in measurement BIPM 2008 consultation date: 2017 www.bipm.org/fr/publications/guides/

[25] de Jonge M D et al 2007 Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form factor of tin over the energy range of 29–60 keV Phys. Rev. A 75 1–14

[26] Cullen D E, Hubbell J H and Kissel L 1997 Epd97: the evaluated photon data library 97 version UCRL-50400 6 consultation date: 2017 www-nds.iaea.org/epd97/

[27] Nordfors B and Noreland E 1961 Ark Fys. 20 1–23

[28] Troussel P and Coron N 2010 BOLUX: a cryogenic electrical-substitution radiometer as high accuracy detector in the 150–11,000 eV range Nucl. Instrum. Methods Phys. Res. A 614 260–70

[29] Ruellan H, Lépy M-C, Etcheverry M, Plagnard J and Morel J 1996 A new spectra processing code applied to the analysis of 235U and 239U in the 60–200 keV energy range Nucl. Instrum. Methods Phys. Res. A 369 651–6

[30] Larkins F B 1977 Semiempirical Auger-electron energies for elements 10 \( \leq Z \leq 100 \) At. Data Nucl. Data Tables 20 311–87

[31] Campbell J L and Papp T 1995 Atomic level widths for x-ray spectrometry X-Ray Spectrom. 24 307–19

[32] Campbell J L and Papp T 2001 Widths of atomic K-N7 levels At. Data Nucl. Data Tables 77 1–56

[33] Salem S I, Tsutsui R T and Rabbani B A 1971 L x-ray transition probabilities in elements with \( Z \leq 57 \) Phys. Rev. A 4 1728–34

[34] Salem S I, Clark D C and Tsutsui R T 1972 L X-ray transition probabilities in elements of medium and high atomic numbers Phys. Rev. A 5 2390–5

[35] McCrary J H, Singman L V, Ziegler L H, Looney L D, Edmonds C M and Harris C E 1972 L fluorescent x-ray relative-intensity measurements Phys. Rev. A 5 1587–91

[36] Scofield J H 1974 Relativistic Hartree–Slater values for K and L x-ray emission rates At. Data Nucl. Data Tables 14 121–37

[37] Bambeynek W, Crasemann B, Fink R W, Freund H–U, Mark H, Swift C D, Price R E and Venugopala Rao P 1972 X-ray fluorescence yields, Auger, and Coster–Kronig transition probabilities Rev. Mod. Phys. 44 716–813

[38] Krause M O 1979 Atomic radiative and radiationless yields for K and L Shells J. Phys. Chem. Ref. Data 8 307–28

[39] McGuire E J 1971 Atomic L–shell Coster–Kronig, Auger, and radiative rates and fluorescence yields for Na-Th Phys. Rev. A 5 587–94