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Improvements and reproducibility of an optimal grazing-incidence position method to L-shell x-ray fluorescence measurements of lead in bone and soft tissue phantoms

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Abstract

L-shell x-ray fluorescence (LXRF) is a non-invasive approach to lead (Pb) concentration measurements in human bone. The method is based on the detection of the characteristic x-ray photons of Pb at 10.5 and 12.6 keV and experimental studies were designed to perform *in vivo* human bone Pb measurements. In later studies, however, the initial LXRF methodology was shown to have poor accuracy and precision. In a recent publication, we investigated an optimal grazing-incidence position (OGIP) approach using a submillimeter x-ray beam from an integrated x-ray tube and polycapillary x-ray lens table-top system. The OGIP method effectively reduced the x-ray scatter and produced a Pb detection limit of $\sim 5 \mu\text{g/g}$ for a 2 mm soft tissue phantom thickness. In this study, the OGIP methodology was improved by using 10 s x-ray spectra acquisitions at sequential positions 0.5 mm apart. The measured Sr K_{α} peak height versus position data was used to spectroscopically identify the bone phantom and the OGIP. The data was fitted with the analytical convolution between a Gaussian and an exponential decay. The position corresponding to the maximum of the fitted convolution function was then selected as the OGIP. Four phantom sets were used. A cylindrical plaster-of-Paris bone phantom doped with Pb in a concentration of $74 \mu\text{g/g}$ was used as a bare bone phantom or with one of the three overlying polyoxymethylene cylindrical shell soft tissue phantoms of 1, 2, and 3 mm thickness. The reproducibility of the OGIP method was assessed in five independent trials using each of the four phantom sets. The coefficient of variation (COV) percentage values of the Sr K_{α} peak height measurements were below 5%. The new procedure decreased by more than threefold the duration and radiation dose of the earlier approach.

Introduction

Lead (Pb) is a well-known toxic element which accumulates in the bone following short- or long-term exposures. Bone Pb comprises about 95% of the entire Pb burden in the human body [1]. Many decades of research on Pb exposures and its negative human health implications led to increased awareness and resulted in Pb-reduction measures and policies in many countries. For example, Pb was eliminated from many common chemicals such as paints and gasoline. However, occupational and accidental Pb exposures still remain areas of public health concern. Moreover, strict adherence to effective codes, regulations, and procedures surrounding the reduction of human Pb exposure is not uniform worldwide. Occupational and childhood Pb exposure in developing countries pose continuous public health hazards. In a relatively recent study, the authors estimated that the burden associated

with childhood Pb exposure amounted to 1.20% of world Gross Domestic Product (GDP) in year 2011 [2]. Clinical studies published in the last two decades also linked developmental problems in children to Pb blood concentrations below 10 µg/dL [3–5].

While most clinical studies use blood Pb concentration for quantitative assessments of human Pb exposures, *in vivo* bone Pb concentration measurement is a better metric of the long-term Pb exposure. The Pb isotope early study of Rabinowitz *et al* [6] estimated the biological half-life of blood Pb to be about 30 d. This time is much shorter than the bone Pb half-life which was estimated to be in the range of years to decades from human bone Pb *in vivo* x-ray fluorescence (XRF) studies [7].

Following the pioneering XRF bone Pb study of Ahlgren *et al* [8], two approaches, denoted herein as LXRF and KXRF, were developed in the early 1980s to measure *in vivo* the Pb concentration in the human bone [7]. LXRF was based on the detection of the Pb L-shell XRF photons [9, 10], while KXRF used the 88 keV γ -ray photons from the ^{109}Cd radionuclide to excite the K-shell electrons of Pb and detect the subsequently emitted XRF photons [11]. The minimal excitation photon energies are just above 15 and 88 keV for LXRF and KXRF, respectively [12]. The KXRF method benefits from an inherently more intense XRF emission. By using a calibration procedure based on the coherent scatter peak, KXRF was also able to account for several experimental factors which introduced significant and varying differences between the bone phantom Pb data and the individual *in vivo* human tibia bone Pb measurements. Such factors were the x-ray attenuation of the overlying soft tissue, patient motion, or bone size. The initial measurement concept strengthened by the improvements and refinements that followed, determined KXRF to be the most widely adopted method for *in vivo* Pb bone measurements [7].

Population bone Pb KXRF measurements found that Pb concentrations in the range from below the detection limit to 20 µg Pb/g-bone mineral for the tibia bone [13]. The KXRF method has seen continuous refinements and improvements since the mid-1980s resulting in lower Pb detection limits. The four-detector KXRF systems developed over a decade ago were reported to have detection limits ~2 µg Pb/g-bone mineral [14, 15].

The LXRF investigations that followed the early studies highlighted problems in the calibration methodology [16]. In short, the early studies did not accurately account for the inherent intra-and inter-individual variations of the Pb LXRF photons x-ray attenuation by the soft tissue overlying the bone. The LXRF Pb concentration measurements in human cadaver tibia bones in the experimental study of Todd *et al* [17] were poorly correlated with the atomic absorption spectrometry measurements.

Despite past difficulties, *in vivo* LXRF bone Pb concentration measurement approach remains appealing. Large population bone Pb surveys in developing countries and rural areas requires low-cost, portable, robust, and time-effective instrumentation. The current KXRF method based on ^{109}Cd does not meet these criteria and, *in vivo* bone Pb surveys are currently conducted by only several research laboratories worldwide. In principle, the ^{109}Cd source can be replaced by a higher voltage (~160 kV) x-ray tube to produce x-ray photons of energies higher than the 88 keV binding energy of the Pb K-shell electrons. However,

miniature x-ray tubes operate at lower voltage values 10–100 kV [18]. Moreover, the direct translation of the KXRF calibration to bone Pb measurements using excitation by a polyenergetic x-ray beam could pose additional difficulties.

Contemporary low-cost x-ray technology comprised of miniature x-ray tubes and silicon-based x-ray detectors continues to improve and penetrate new areas of applied science and technology. Combined with practical x-ray optics devices, such as polycapillary x-ray lenses [19], portable and table-top x-ray devices [20, 21] have become increasingly common in many XRF, x-ray diffraction, and x-ray imaging applications in the 1–50 keV x-ray photon energy range.

In recent years, the new x-ray technologies were also tested in bone Pb LXRF studies. Portable XRF devices, in particular, were investigated as potential instruments for Pb bone detection. Fleming *et al* [22] used a portable XRF device and Pb-doped plaster of Paris (poP) bone phantoms with and without soft tissue phantom attenuation. The authors found Pb detection limits in the 7–43 $\mu\text{g/g}$ range depending on the phantom shape and soft tissue phantom thickness. Nie *et al* [23] found a Pb detection limit of 8.4 $\mu\text{g/g}$ with a 2 mm soft tissue thickness, a good correlation with KXRF measurements, and developed a new spectrometric method to measure soft tissue thickness. Further, Specht *et al* [24] used two portable XRF devices on goat and cadaver bones to develop a new spectrometric calibration approach to *in vivo* Pb LXRF measurements labeled background subtraction. The approach did not include the traditional XRF peak fitting procedure, but exploited the differences in the acquired spectra which were correlated with the Pb concentration of the samples. Using their new calibration method, the authors found a Pb detection limit of 2.9 $\mu\text{g/g}$ for a set of Pb-doped phantoms and 2 mm thick Lucite (soft tissue substitute).

Gherase and Al-Hamdani investigated in a recent publication an optimal grazing-incidence position (OGIP) approach to the bone Pb LXRF measurements using the sub-millimeter x-ray beam produced by an integrated x-ray tube and x-ray lens table-top system [25]. Measurements of the Pb concentration in a small volume ($\sim 1 \text{ mm}^3$) within the superficial 1–2 mm depth of the outer cortical bone tissue is clinically relevant. Several synchrotron XRF microscopy studies of human bone samples indicated elevated Pb concentrations in the outer cortical bone tissue [26–29].

The experimental conditions of Gherase and Al-Hamdani study [25] did not meet the requirements of traditional grazing-incidence XRF experiments whereas the angle between the incident beam and sample surface is very small approaching the critical angle of total reflection of only a few milliradians. However, the experimental results demonstrated that the OGIP effectively mitigated the negative effect of the scattered photons on the Pb detectability [25]. Using five 180 s trials, a Pb detection limit of $\sim 5 \mu\text{g/g}$ was found corresponding to a 2 mm layer of polyoxymethylene (POM) overlying the poP Pb-doped bone phantoms. Strontium (Sr) was a contaminant of the commercial poP and its K_{α} peak height measurement was used to find the OGIP.

Within the *ad-hoc* experimental procedures employed in the OGIP approach, two problems were identified. First, the step size of the phantom position was varied in the 0.1–0.5 mm

range in order to identify the OGIP with sufficient accuracy. Combined with the 30 s x-ray spectrum acquisition selected for each position, the time required to find the OGIP for a 0.1 mm step size and a 3 mm range can be calculated to be 15 minutes – five times the duration of each Pb measurement trial. Thus, there was a relatively high cost for the overall time measurement and radiation exposure within the OGIP method. Second, significant deviations from linearity were observed in the Pb calibration data for the bare bone phantoms. While bone phantom density variation was invoked as a potential origin, the authors later considered that reproducibility issues with the OGIP procedure could have affected the outcomes [25].

Methods

In this study, the procedure employed by Gherase and Al-Hamdani [25] was improved and consisted of 10 s x-ray spectra acquisitions at sequential phantom positions in 0.5 mm steps. Four phantom sets were made of one poP bone phantom doped with Pb (74 µg/g concentration) used as bare bone phantom and with three overlying soft tissue phantoms made of POM cylindrical shell sections of 1, 2, and 3 mm thickness. The soft and bone tissue phantoms were designed to simulate the frontal middle part of human tibia bone and the overlying soft tissue. This anatomical location was used in the past KXRF and LXRF Pb bone measurements [11], [14], [17]. The Sr K_{α} peak height measurements versus position data was fitted by an analytical function which was calculated as the convolution between Gaussian and exponential attenuation functions. The position corresponding to the maximum value of the fitted function was selected as the OGIP. Following phantom positioning at the OGIP, three 300 s spectra were subsequently acquired.

Five independent experimental trials were taken to assess the reproducibility of the new developed OGIP method for each phantom. Each trial started with the initial positioning of the phantom on the XY stage by hand. The peak height measurements at the OGIP demonstrated good reproducibility of the method. The coefficient of variation (COV) percentage values of the Sr K_{α} peak height measurements were less than 5% across all four phantoms. The chi-squared test indicated large differences among the five trial data at the 5% significance level. These variations corresponded to the XRF peaks for which the average relative uncertainty of individual trials was at the ~1% level. In the *Discussion* section, possible origins of these observed differences were indicated in the context of the specific experimental procedures employed in this study. In the same section, the parameter values resulting from the convolution fitting were also qualitatively discussed.

Materials

Polyoxymethylene (POM) plastic and plaster of Paris (poP) were used as soft tissue and bone phantom materials, respectively. Their chemical formulae and density values are provided in table 1. These are common phantom materials used in numerous medical x-ray applications and studies. In section 4, the quantitative discussion and interpretation of the results was based on the x-ray linear attenuation coefficients (μ) of the poP and POM phantom materials. A closely related material parameter is the inverse of the linear

attenuation coefficient (μ^{-1}). This is interpreted as the material thickness for which the number of x-ray photons at normal incidence decreases by a factor of $1/e$ (or 36.8%).

In a stochastic interpretation, μ^{-1} is the average distance the photon travels in the material between two consecutive interactions and it is also referred to as the mean-free-path (MFP). The x-ray attenuation parameters are provided in table 2.

The linear attenuation coefficients (μ) of table 2 were calculated using XCOM online x-ray photon cross section database of the National Institute of Standards and Technology (NIST) [30]. The chemical formulas and density values of the poP and POM phantom materials were provided in table 1. The average soft tissue elemental composition and 1.06 g/cm^3 density were taken from the Report 44 of the International Commission on Radiation Units and Measurements (ICRU-44) [31].

Phantom preparation

The fabrication of the bone and soft tissue phantoms was detailed in our previous publication [25]. However, for clarity, a description of procedures is included in the following sentences. The poP in powder form (Sigma-Aldrich, St. Louis, MO, US) was mixed with distilled water and doped with a known volume of Pb standard atomic absorption solution with a Pb concentration of $(1000 \pm 4) \text{ mg/L}$ (Sigma-Aldrich, St. Louis, MO, US). The mixture was then poured into an aluminum (Al) cylindrical mold with a 29 mm inner diameter. Solidification of the poP mixture produced a cylindrical bone phantom. Its Pb concentration and density were calculated based on the initial Pb mass and final mass and volume measurements of the bone phantom. In this study, a single bone phantom with the $74 \text{ }\mu\text{g/g}$ Pb concentration was used. The POM soft tissue phantoms were machined in three cylindrical shells with 1, 2, and 3 mm thickness and 30 mm inner diameter. For a smooth gapless contact between the poP and POM phantoms, the cylindrical poP bone phantom surface was gently polished with a fine sandpaper. The cylindrical shell POM soft tissue phantom was cut in two places along its length such that its cross section was less than half of the initial circular shell, as shown in the schematic of figure 1. The abbreviations of the four bone and soft tissue phantom assemblies were: bb, bb-1mm, bb-2mm, and bb-3mm, indicating $74 \text{ }\mu\text{g/g}$ Pb poP bare bone, and bare bone and 1, 2, and 3 mm thickness POM phantoms, respectively.

Experimental setup

The detailed schematic of the experimental setup used in this study is shown in figure 1. It is important to note that the schematic was drawn to scale using CorelDRAW Graphics Suite X8 software (Corel Co, Ottawa, ON, Canada). The x-ray beam was produced by an integrated x-ray tube and polycapillary x-ray lens (PXL) (Polycapillary X-beam PowerFlux model, X-ray Optical Systems, Inc., East Greenbush, NY, US). The x-ray tube had a tungsten (W) target and the x-ray lens was 10 cm in length and 1 cm outer diameter. The x-ray tube voltage and current could be varied in 0.1 kV and 1 μA increments, respectively. Their maximum values of 50 kV and 1 mA were used during the LXRF measurements. Knife-edge x-ray beam size measurements performed in our lab determined that the x-ray lens had a focal length of 4 mm (f_{PXL} in figure 1) where the x-ray beam had a $24 \text{ }\mu\text{m}$ lateral

size measured as full width at half-maximum (FWHM) at the 10 keV photon energy [32]. At the 10 keV photon energy, the x-ray beam divergence measured at a distance larger than the 4 mm focal length was 7.8 mrad (or 0.45°). Using these measurements, the FWHM of the x-ray beam at the distance $d_{fd} = 11$ mm between the PXL focal point and the detector axis, was calculated to be ~0.2 mm. The PXL x-ray beam was filtered using an eight-slot wheel in which custom-made filters could be placed. A 1.8 mm thick Al filter was used to attenuate the W L-shell XRF emissions in the 8–12 keV energy range.

X-ray photon counting and energy measurements (i.e. x-ray spectra acquisition) were accomplished using a silicon-drift x-ray detector with integrated pulse-height analyzer (X-123 SDD, Amptek, Bedford, MA, US). The circular active area of the detector was 25 mm² (or 5.6 mm diameter) and 0.5 mm thickness and the window was a 12.7 µm-thickness beryllium (Be) sheet. The counting rate capability of the detector provided by the manufacturer was 10⁵ counts/s. For all x-ray spectra acquisitions, the dead time/real time percentage ratios were less than 5%.

The entire XRF setup was placed on an x-ray shield consisting of a 56×62 cm² and 6.35 mm-thickness Al plate. The plate was covered by a stainless steel box with a slightly smaller base area and 46 cm in height which could be manually opened to allow operating access to the XRF setup when the x-ray beam was turned off. The integrated x-ray tube and PXL unit was mounted in a fixed position inside the x-ray shield. The integrated x-ray tube and PXL unit was also equipped with an electromechanical beam shutter and a green and yellow light beacon which indicated the on or off status of the x-ray beam. The cables connecting the devices within the x-ray shield with the controlling laptop and the power supply devices were guided through two L-shaped metallic pipes. The entire x-ray shield was mounted on an optical table (Newport, Irving, CA, US) which also served as mechanical support for the laptop and the x-ray tube power supply. The operator radiation exposure rates outside the shielding were at the natural background levels as periodically verified using a calibrated Geiger-Müller counter (model 3 survey meter, Ludlum Measurements Inc., Sweetwater, TX, US).

Experimental procedures

During the experiments, the POM soft tissue phantom was secured on the poP cylindrical bone phantom with a rubber band below the x-ray beam (not shown in the figure 1). The phantom assembly was placed by hand on an automated XY modular motorized linear positioning stage assembly (Newport, Irvine, CA, US). Sample positions with a 1 µm accuracy could be achieved with this system. The detector and the XY positioning stage were kept at the same position relative the fixed position of the x-ray beam during the experiments such. The x-ray detector was positioned such that its window was parallel to the direction of the x-ray beam as shown in figure 1. The detector position was secured using a magnetic base support.

For each of the four bone and soft tissue phantom sets (bb, bb-1mm, bb-2mm, bb-3mm), five repeated experimental data sets were acquired. In each trial, x-ray spectra acquired at various phantom position along the x-axis (as in figure 1) were analyzed and used to determine the optimal position of the phantom. Before each trial, the phantom was placed by hand on the

XY positioning stage such that its circular outer surface is tangent to the estimated direction of the x-ray beam, but with the x-ray beam not incident on the sample. To enhance reproducibility, the edges of the Al collimator were used as a visual guide. The precise position of the phantom on the x -axis with respect to the x-ray beam location was not known. The phantom was positioned by the stage on the x -axis in sequential 0.5 mm steps towards the x-ray detector. At each position one 10 s (real time) x-ray spectrum was acquired. The number of counts at one channel centered on the Sr K_{α} peak was monitored as the x-ray spectra were acquired. The sequence of these values was used to determine if additional steps were required. As expected, a larger number of steps were required for the thicker soft tissue phantoms bb-2mm and bb-3mm. The acquired spectra were analyzed to measure the Sr K_{α} peak height for each relative phantom position. The peak fitting methods are described in the *Data Analysis* section.

The Sr K_{α} peak height versus relative position data was fitted with a function (x) calculated as a convolution between normalized (i.e. area under the curve equal to unity) Gaussian (x) and exponential attenuation $h(x)$ functions. These functions described the x-ray beam intensity profile and the x-ray attenuation in the bone and soft tissue phantoms, respectively. Further details of the analytical calculations are provided in the Appendix section. The position corresponding to the maximum of the fitted convolution function was determined graphically using the data reader tool in the OriginPro 2018 software. This position was then selected as the OGIP. The phantom was re-positioned at OGIP and three repeated 300 s (real time) x-ray spectra Page 9 of 21 were acquired. All the observed XRF peaks were fitted using OriginPro 2018 software and then data was plotted and interpreted.

Sr was a contaminant of the poP product and it was assumed to be uniformly-distributed within the bb phantom. Its concentration in the bb phantom used in this study was not known or measured. However, Sr concentration was assumed to be about one magnitude larger than the measured 74 $\mu\text{g/g}$ Pb concentration. Using poP chemical formula from table 1, the 74 $\mu\text{g/g}$ Pb concentration can be converted to a 0.27 mg Pb/g Ca. In a commercial poP product, Pejović-Milić *et al* [33] measured a concentration of 4 mg Sr/g Ca. Hence, short-time (10 s) acquisition spectra were sufficient to determine the optimal bone phantom positions as in our previous study [25]. Sr K-edge and Pb L_3 -edge energies are relatively close at 13.0 and 16.1 keV, as provided in the first two columns of table 2. Therefore, the OGIP measured using the Sr K_{α} peak was selected as a substitute of the OGIP corresponding to the Pb LXRF detection.

Data analysis

The raw x-ray spectra were analyzed using OriginPro 2018 (OriginLab Northampton, MA, US) statistical data analysis and plotting software. The Pb L_{α} and Pb L_{β} peaks were fitted separately by selecting only the data around the peaks. All XRF peaks were modeled as a Gaussian function with a linear background according to the following equation:

$$y = a + bx + \text{Hexp} \left[-\frac{(x - x_0)^2}{2\sigma^2} \right] \quad (1)$$

In equation (1), variables y and x represent the number of counts and photon energy, respectively. The variables a and b are the parameters of the linearly-modelled background, and H , x_0 , and σ are the peak height, center, and standard deviation parameters of the Gaussian peak model, respectively. The observed Sr K_α and Sr K_β , as well as the Ca K_α and Ca K_β peaks (which were observed for the bare bone (bb) phantoms) were fitted simultaneously using a model as in equation (1) to which a second Gaussian function was added. For each channel with N counts, the standard deviation of the measurement was taken to be equal to $\sqrt{N}$ according to the Poisson statistics. Thus, the corresponding statistical weight was equal to $1/N$. Goodness-of-fit of the peak fitting procedure was simultaneously monitored using the reduced chi-square value (χ^2/n), and visualization of the fitted function and data plots. X-ray atomic transitions of the observed XRF peaks were identified using the tabulated data from Deslattes *et al* [12]. Data plotting was also performed using the OriginPro 2018 software.

The results at the OGIP were presented as the mean and standard deviation of the three peak height measurements obtained in the 300 s trials. Reproducibility of the grazing-incidence experimental method was assessed by fitting with a constant the observed XRF peak height weighted average values obtained in the five repeated trials. Finding the fitted constant value, its error, and the corresponding reduced chi-squared ($\chi^2/4$) value, did not require a numerical minimization algorithm, and were calculated using analytical equations [34]. These calculations and organization of the final results were performed using Microsoft Office Excel software (Microsoft, Redmond, WA, US). A chi-squared test at the 5% statistical significance level was performed to decide if the higher than unity $\chi^2/4$ value indicated significant variations in any of the five-trial peak height data sets (i.e. significant departure from reproducibility). For the four degrees of freedom, a $\chi^2/4$ value larger than 2.4 corresponded to a p -value lower than 5%. The 2.4 value was interpolated from the tabulated percentage probability values of the chi-squared distribution function from the Taylor textbook [34].

Convolution function

The function (x) that was used to fit the peak height versus the relative phantom position data. It was calculated as the convolution between normalized Gaussian function (x) and normalized exponential attenuation function $h(x)$ and then multiplied by an “amplitude” constant A :

$$f(x) = A \cdot [g(x) * h(x)] \stackrel{\text{def}}{=} A \int_{-\infty}^{+\infty} g(t)h(x-t)dt = A \int_{-\infty}^{+\infty} h(t)g(x-t)dt \quad (2)$$

The expressions of the normalized functions (x) and $h(x)$ are provided in the equations (3) and (4) below.

$$g(x) = \frac{1}{w\sqrt{2\pi}} \exp\left[-\frac{(x-x_0)^2}{2w^2}\right] \quad (3)$$

$$h(x) = \begin{cases} 0, & x < 0 \\ \mu e^{-\mu x}, & x \geq 0 \end{cases} \quad (4)$$

The x_0 and w parameters represent the center and standard deviation of the Gaussian function $g(x)$, while μ represents the linear attenuation coefficient of the normalized exponential attenuation function $h(x)$. Additional details on the physical meaning of these parameters are provided in the *Discussion* section.

The analytical result of the convolution operation described in equation (2) is given in the equation (5). Details of its derivation were summarized in the Appendix section.

$$f(x) = A \frac{\mu}{2} \exp\left(-\frac{\mu^2 w^2}{2}\right) \exp(-\sqrt{2}\mu w z) [1 + \operatorname{erf}(z)], \quad (5)$$

In equation (5), $\operatorname{erf}(x)$ denotes the well-known error function. The notation $z = (x - x_0 - \mu w^2)(\sqrt{2}w)$ was used to simplify the mathematical expression of $f(x)$. Fitting the function (x) to the data was performed using the OriginPro software. A custom-built fitting function based on the mathematical expression from equation (5) was written using the OriginPro user-defined fitting function tool.

Results

Sample plots of the x-ray spectra obtained for the bb and bb-3mm phantoms are shown in figure 2. It is important to notice the x-ray attenuation of the overlying POM soft tissue phantom affecting all observed XRF peaks. The lower energy XRF peaks of sulphur (S) and calcium (Ca) were not observed in any of the x-ray spectra corresponding to the bb-1mm, bb-2mm, and bb-3mm phantoms. The continuous curves in the inset plot of figure 2(a) show a sample fitting of the Pb L_{α} and Pb L_{β} peaks. The figure 2(a) and 2(b) plots also show the larger scattered bremsstrahlung of the bb-3mm phantom (red line) comparing to the that of the bb phantom (black line). The observed difference was due to the larger number of x-ray photons scattered within the POM layer that were able to reach the detector versus the lower number of x-ray photons that were not absorbed following scattering events within the poP material.

Figure 3 shows sample plots and convolution function (x) fitting of the peak height versus the relative phantom position data. Sr K_{α} peak height data is shown for all four phantoms,

while Ca K_{α} and Ca K_{β} data is only shown for the bb phantom where the two peaks were observed.

The progressively stronger x-ray attenuation of the Sr K_{α} peak height data with the increasing POM layer thickness was highlighted using a common y-axis scale of the top four graphs. The shift towards the right of the maximum value of the fitted convolution function also increased with increasing POM phantom thickness.

The values and associated uncertainties of the convolution function fitting parameters w and μ for the four phantoms are summarized in table 3. The weighted average values of the A and x_0 parameters were not provided, given they did not have relevant physical significance. The x_0 values depended on the initial random position of the phantom on the x -axis of figure 1. Therefore, the x_0 values were significantly different for each five-trial set and amongst the trials conducted with the four different phantoms. The A parameter values indirectly depended on the thickness of the POM phantom.

The Sr K_{α} peak height data was used for all phantoms, while Ca K_{α} was only available for the bb phantom. The peak height data for the observed XRF lines of P, S, Ca, Pb, and Sr in the x-ray spectra acquired at the optimal position for all five trials is provided in figures 4(a)-(d) and in table 4.

In the plots of figures 4a-d, departures from a constant value can be noticed at the 5% statistical significance level (i.e. > 2.4). These are indicated by the p -values lower than 5% in the fifth column of table 4 and include the Ca K_{α} and S K_{α} data for the bb phantom and the Sr K_{α} peak data for the remaining three phantoms. In those measurements, the individual trial measurement uncertainties (error bars in the plots of figures 4a-d) were smaller than the standard deviation of the five trial data. For example, in a single bb phantom trial, the average relative uncertainty of the Ca K_{α} peak height measurement was around 0.7%. By comparison, its five trial COV percentage value was 3.4% which is almost 5 times larger than average individual trial uncertainty. Hence, there were uncertainties in the five trial data which were not included in the individual trial error bars. The possible origins of these uncertainties are provided in the first paragraphs of the *Discussion* section.

The last column of table 4 indicates that most peak height measurements had a COV below 10%, and the data of the most intense peaks had even a COV below 5%. This indicates a good reproducibility of finding the OGIP. Exceptions from the COV<10% observation were the peak height measurements of the Pb L_{α} and Pb L_{β} peaks. However, the larger relative standard deviation is not related to unaccounted measurement errors. It can be simply explained by the relatively small peak height values of Pb LXRF lines and the Poisson statistics governing the number of detected photons per channel. For a number N of detected photons, the Poisson relative standard deviation is equal to $1/\sqrt{N}$. Thus, for $N=10$, its Poisson relative standard deviation is about 32%.

Discussion

Overall, the optimal grazing-incidence geometry data sets shown in the plots of figures 4a-d demonstrate a good reproducibility of the experimental methodology employed using the

four bone and soft tissue phantoms. However, peak height data of the most intense observed XRF peaks, summarized in table 4, indicated that certain intrinsic experimental factors affected the experimental reproducibility. Some of these factors are explained in detail in the following paragraphs.

Small deviations from the precise XRF geometry shown in figure 1 likely occurred in the initial phantom placement by hand on the XY positioning stage. For example, the point on the circular phantom edge on which the detector axis is perpendicular might not have coincided with the point on which the detector axis is perpendicular on the circular phantom edge. Also, the point on the circular phantom edge tangent to the direction of the x-ray beam was likely not precisely in the same position along the x-ray beam. This could have affected the measurements in two ways. First, the effective x-ray beam size could have varied during each trial. Since the x-ray beam divergence is small (0.45° at 10 keV energy), it can be deduced that the effective x-ray beam size variations were relatively small. Second, the positioning error could have affected the outcome of each trial due to the presence of small local variations in the density and elemental composition of the poP bone phantom.

Another potential contributing factor was the observed variation of the POM soft tissue phantom thickness. This originated during the machining process of the POM phantoms. Vernier caliper thickness measurements in various points showed variations up to 0.1 mm. Since the location of the circular POM edge tangent to the direction of the beam was about the same in all trials, thickness variations around that particular location were likely not as large as 0.1 mm. However, the incident x-ray beam is tangent to the soft tissue phantom, and, therefore, crosses a larger POM thickness. Hence, thickness variations of up to 0.05 mm, which are equivalent to 5% relative errors for the bb-1mm phantom, can translate into larger x-ray attenuation variations, which, determined, in part, the five trial relative standard deviation values from the last column of table 4.

Table 3 provides the weighted average values of the w and μ parameters obtained by the convolution function data fitting procedure. A precise physical interpretation of these parameters requires an accurate modelling of the x-ray interactions involved in these experiments. Such modelling is outside the main goal and scope of this study.

The OGIP methodology employed in this study significantly reduced the total x-ray exposure and data acquisition times reported in our previous study [25]. In the previous approach, the precision of finding the OGIP was strongly dependent on the step size in the phantom positioning sequence. A step size as low as 0.1 mm was required to obtain accurate OGIP results. By employing the convolution fitting procedure, a step size of 0.5 mm was sufficient to preserve the accuracy of the method. Moreover, the x-ray spectrum acquisition time during the sequence was reduced from 30 s to only 10 s. Thus, a comparable precision was achieved in this study using acquisition times which, compared to our previous OGIP procedures, were shorter by a factor in the range of 3 to 15. For *in vivo* bone Pb applications, further reduction of time and associated radiation dose is still possible by using soft tissue thickness estimates which could better guide the initial bone edge position relative to the x-ray beam direction. These estimates can be obtained from additional ultrasound

measurements as employed in previous Pb bone LXRF studies [10], or from approximate inferences with patient-specific data such as sex, age, and body mass index.

An important research development in bringing this OGIP method closer to *in vivo* bone Pb measurements would be the use of the scattered bremsstrahlung data instead of the Sr peaks. In the unexposed human bone, the Sr concentration are expected to be in the 0.1–0.3 mg Sr/g Ca which is roughly more than 10 times lower than the Sr concentration in the poP bone phantom used in this study [33]. The peak height Sr K_{α} measurement for the bb-3mm phantom during the 10 s and 0.5 mm data acquisition procedure is ~10 counts as shown in the middle-right sample panel plot of figure 3. A peak height 10 times lower would be at, or below, the detection limit. Therefore, a different approach could be used for *in vivo* applications. A possible direction of study is the analysis of the broad bremsstrahlung data from the x-ray spectra acquired in the OGIP finding procedure.

Conclusions

In a study published recently, an optimal grazing-incidence position (OGIP) L-shell XRF (LXRF) approach to detection of Pb in bone and soft tissue phantoms demonstrated early promising results: ~5 µg/g Pb detection limit was measured for a 2 mm soft tissue thickness. In this study, an improved OGIP methodology was developed and its reproducibility was assessed. Four phantom sets consisting of a 74 µg/g Pb-doped bone phantom and three soft tissue phantoms of 1, 2, and 3 mm thickness were used. Each bone and soft tissue phantom was sequentially positioned towards the x-ray beam in 0.5 mm steps. A single x-ray spectrum was acquired in 10 seconds at each position. The analytical convolution function between a Gaussian and an exponential attenuation was used to fit the Sr K_{α} peak height versus position data. The position corresponding to the maximum of the function was selected as the OGIP. Good reproducibility of the new OGIP method was found from the data analysis of five independent trials. Coefficient of variation percentage values of the Sr K_{α} peak height measurements were below 5% for all four phantom sets. The new method also reduced the time and associated radiation dose of the initial approach by more than threefold.

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Appendix

The convolution function (x) is defined by the following integral:

$$f(x) = A \cdot [g(x) * h(x)] \stackrel{\text{def}}{=} A \int_{-\infty}^{+\infty} g(t)h(x-t)dt \quad (A1)$$

The Gaussian function (x) and the exponential attenuation function $h(x)$ were defined in their normalized forms (area under their curve equal to unity):

$$g(x) = \frac{1}{w\sqrt{2\pi}} \exp\left[-\frac{(x-x_0)^2}{2w^2}\right] \quad (\text{A2})$$

$$h(x) = \begin{cases} 0, & x < 0, \\ \mu e^{-\mu x}, & x \geq 0. \end{cases} \quad (\text{A3})$$

Then,

$$h(x-t) = \begin{cases} 0, & x-t < 0 \\ \mu e^{-\mu(x-t)}, & x-t \geq 0 \end{cases} = \begin{cases} 0, & t > x \\ \mu e^{\mu t} e^{-\mu x}, & t \leq x \end{cases} \quad (\text{A4})$$

It follows that the integral from equation (A1) can be written as:

$$f(x) = A \int_{-\infty}^x g(t) \mu e^{-\mu x} e^{\mu t} dt = \frac{\mu e^{-\mu x}}{w\sqrt{2\pi}} \int_{-\infty}^x \exp\left\{-\left[\left(\frac{t-x_0}{w\sqrt{2}}\right)^2 - \mu t\right]\right\} dt \quad (\text{A5})$$

The exponent expression in the integral from equation (A5) can be written as a binomial in t :

$$\left(\frac{t-x_0}{w\sqrt{2}}\right)^2 - \mu t = \frac{1}{2w^2} [t - (x_0 + \mu w^2)]^2 - \left(x_0 \mu + \frac{\mu^2 w^2}{2}\right) \quad (\text{A6})$$

A change of variables can be performed in the integral from equation (A5) as follows:

$$y = \frac{t - (x_0 + \mu w^2)}{w\sqrt{2}} \Rightarrow dt = \sqrt{2} w dy \quad (\text{A7})$$

The convolution function (x) is, then, given by:

$$f(x) = \mu \exp\left[-\mu(x-x_0) + \mu^2 w^2 / 2\right] \int_{-\infty}^z \frac{1}{\sqrt{\pi}} e^{-y^2} dy \quad (\text{A8})$$

The upper limit z of the integral in equation (A7) is a notation resulting from the change of variable:

$$z = \frac{x - x_0 - \mu w^2}{w\sqrt{2}} \quad (\text{A9})$$

The integral of equation (A7) can also be further simplified as follows:

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^z e^{-y^2} dy = \frac{1}{\sqrt{\pi}} \left(\int_{-\infty}^0 e^{-y^2} dy + \int_0^z e^{-y^2} dy \right) = \frac{1}{2} [1 + \operatorname{erf}(z)] \quad (\text{A10})$$

In equation (A9) the notation $\operatorname{erf}(z)$ denotes the well-known error function which is defined as:

$$\operatorname{erf}(z) \stackrel{\text{def}}{=} \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy \quad (\text{A11})$$

Following a few algebraic manipulations involving the z notation from equation (A8) and the results of equations (A7) and (A9), the final expression of the convolution function is:

$$f(x) = \frac{\mu}{2} \exp \left[- \left(\frac{\mu^2 w^2}{2} + \mu w z \sqrt{2} \right) \right] \cdot [1 + \operatorname{erf}(z)]. \quad (\text{A12})$$

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Figure 1. Schematic of the experimental setup with a bb-2mm phantom. Legend and relevant dimensions and distances are provided. The scale of the drawing is shown in the bottom left corner.

Figure 2.

Sample plots of the x-ray spectra: 300-s x-ray spectra of the bb and bb-3mm phantoms at the OGIP in the 0–40 keV (a) and 9.5–13.5 keV (b) energy ranges, 10-s x-ray spectra of the bb and bb-3mm phantoms at the intermediate relative positions of 2.5 mm and 3.5 mm, respectively in the 0–40 keV (c) and 13.5–16.5 keV (d) energy ranges.

Figure 3.

Sample plots of the peak height versus the relative position of the phantom. Continuous red lines represent the best fit curves of the convolution function (x). Best fit parameters, associated uncertainty, and reduced chi-squared (χ^2/n) values are provided for each plot. Sr K α peak height data sample plots for the four phantoms are shown in the top four panels and Ca K α and Ca K β peak height data sample plots are shown in the bottom left and right panels, respectively.

Figure 4a.

Plots of the five-trial P, S, Ca, Pb, and Sr fitted peak height values acquired with the bb phantom at the optimal grazing-incidence positions.

Figure 4b.

Plots of the five-trial Pb and Sr fitted peak height values acquired with the bb-1mm phantom at the optimal grazing-incidence positions.

Figure 4c.

Plots of the five-trial Pb and Sr fitted peak height values acquired with the bb-2mm phantom at the optimal grazing-incidence positions.

Figure 4d.

Plots of the five-trial Pb and Sr fitted peak height values acquired with the bb-3mm phantom at the optimal grazing-incidence positions.

Table 1.

Chemical formulas and density values of the two phantom materials. The digit in the round parentheses in the last column is the experimental uncertainty on the last significant figure.

Phantom material	Abbreviation	Tissue substitute	Chemical formula	Density (g/cm ³)
Polyoxymethylene	POM	Soft tissue	(CH ₂ O) _n	1.5(1)
Plaster of Paris	poP	Bone	CaSO ₄ · 1/2 H ₂ O	0.99(6)

Table 2.

X-ray photon attenuation properties of the POM and poP phantom materials. The $\left(\frac{\mu}{\rho}\right)$, μ and μ^{-1} symbols represent the x-ray photon mass attenuation coefficient, the linear attenuation coefficient, and the mean-free-path, respectively. The numbers in the round parentheses are the uncertainties on the second significant figure and they were calculated using error propagation of the density uncertainty values from table 1. The soft tissue (ICRU-44) data was added for comparison with the data of the POM material

		poP			POM			Soft tissue (ICRU-44)		
Photon energy (keV)	Significance	$\left(\frac{\mu}{\rho}\right)(\text{cm}^2/\text{g})$	$\mu(\text{mm}^{-1})$	$\mu^{-1}(\text{mm})$	$\left(\frac{\mu}{\rho}\right)(\text{cm}^2/\text{g})$	$\mu(\text{mm}^{-1})$	$\mu^{-1}(\text{mm})$	$\left(\frac{\mu}{\rho}\right)(\text{cm}^2/\text{g})$	$\mu(\text{mm}^{-1})$	$\mu^{-1}(\text{mm})$
3.7	Ca K_{α}	272.4	27(2)	0.037(3)	81.70	12(1)	0.083(7)	102.60	10.88	0.092
4.0	Ca K_{β}	219.9	22(1)	0.046(2)	64.78	9.8(9)	0.102(9)	81.60	8.65	0.116
4.1	Ca K-edge	460.5	46(3)	0.022(1)	62.42	9.5(9)	0.10(1)	75.89	8.04	0.124
10.5	Pb L_{α}	34.69	3.4(2)	0.29(2)	3.60	0.55(5)	1.8(2)	4.66	0.49	2.023
12.6	Pb L_{β}	20.67	2.1(1)	0.48(2)	2.13	0.32(3)	3.1(3)	2.76	0.29	3.423
13.0	Pb L_{3} -edge	18.91	1.9(1)	0.53(3)	1.95	0.30(3)	3.3(3)	2.52	0.27	3.739
14.1	Sr K_{α}	15.00	1.49(9)	0.67(4)	1.56	0.24(2)	4.2(3)	2.01	0.21	4.689
15.8	Sr K_{β}	10.83	1.07(7)	0.93(6)	1.16	0.18(2)	5.6(6)	1.48	0.16	6.379
16.1	Sr K-edge	10.26	1.02(6)	0.98(6)	1.11	0.17(2)	5.9(7)	1.41	0.15	6.700

Table 3.

Weighted average values of the w , μ , and A parameters obtained from the convolution function fitting of the five-trial data for the four phantom set.

Phantom	bb	bb-1mm	bb-2mm	bb-3mm	bb	bb
Parameter	Sr K_{α}				Ca K_{α}	Ca K_{β}
w (mm)	0.68(2)	0.81(7)	0.58(6)	0.7(1)	0.56(2)	0.62(4)
μ (mm ⁻¹)	0.9(1)	0.49(8)	0.24(4)	0.27(3)	0.95(9)	0.7(2)

Table 4.

Table of the reduced chi-squared value (χ^2/n), the percentage p -value relative to the 5% significance level, and the COV percentage values corresponding to the five-trial peak height data. The element and atomic transition for each peak are also provided.

Phantom	Element	Atomic transition	χ^2/n	p -value (%)	Mean (counts)	SD (counts)	COV (%)
bb	P	K $_{\alpha}$	0.8	>5	42	2	4.8
	S	K $_{\alpha}$	2.6	<5	344	10	2.9
		K $_{\beta}$	1.4	>5	25	3	12.0
	Ca	K $_{\alpha}$	30.2	<5	3337	114	3.4
		K $_{\beta}$	3.8	<5	498	16	3.1
	Pb	L $_{\alpha}$	0.4	>5	29	1	3.5
		L $_{\beta}$	1.2	>5	26	2	7.7
	Sr	K $_{\alpha}$	1.5	>5	1138	11	1.0
		K $_{\beta}$	2.2	>5	173	7	4.0
bb-1mm	Pb	L $_{\alpha}$	2.2	>5	10	1	10.0
		L $_{\beta}$	1.3	>5	13	2	15.4
	Sr	K $_{\alpha}$	13.3	<5	488	21	4.3
		K $_{\beta}$	1.1	>5	82	4	4.9
bb-2mm	Pb	L $_{\alpha}$	2.4	>5	7	1	14.3
		L $_{\beta}$	0.3	>5	10	1	10.0
	Sr	K $_{\alpha}$	7.6	<5	355	14	3.9
		K $_{\beta}$	0.8	>5	64	4	6.3
bb-3mm	Pb	L $_{\alpha}$	2.1	>5	4	1	25.0
		L $_{\beta}$	1.5	>5	8	2	25.0
	Sr	K $_{\alpha}$	6.3	<5	243	12	4.9
		K $_{\beta}$	1.1	>5	51	4	7.8