Monte Carlo modeling and application study of Hybrid L-Edge/L-XRF densitometry

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Abstract

Precise measurement of uranium (U) and plutonium (Pu) concentrations is critical in spent nuclear fuel reprocessing for nuclear material accounting and process control. The hybrid L-edge/L-XRF densitometry (HLED), which combines the L-edge densitometry technique with the X-ray fluorescence (XRF) technique, can be applied to measure the concentration of U and Pu in both pure and mixed forms. In this study, a Geant4-based simulation model of the HLED system was established to optimize critical parameters including X-ray tube voltage, primary filter configuration, XRF detection angle and collimator design. The simulation results reveal that the optimal parameters for the X-ray tube are an X-ray source voltage of 30 kV and a 0.15 mm Ni filter, with an XRF detection angle of 45°. An HLED platform was also developed based on the simulation model for practical validation. The working curve was calibrated using standard uranium samples spanning a concentration range of 14 g/L to 162 g/L, yielding a coefficient of determination (R2) of 0.999. Measurement validation showed relative errors of less than 2% and measurement precision of less than 0.5%. To address the low measurement precision for both low-concentration samples that produce weak L-edge absorption, and high-concentration samples that exhibit strong L-edge absorption, an optimal path length and a current correction model of X-ray tube were presented, respectively. Furthermore, a uranium solution of 1.807 g/L and a thorium (Th) solution of 200 g/L was prepared to verify the precision performance. The experimental results indicate that the measurement precision of the 1.807 g/L uranium solution can be improved from 2.356% to 1.588% by increasing the path length. An optimal path length of 11 mm for samples with concentration below 10 g/L was obtained by simulation experiment. Moreover, the precision of the 200 g/L thorium solution was increased by 35%, with relative standard deviation decreasing from 2.35% to 1.588%.

Full Text

Preamble

Monte Carlo modeling and application study of hybrid L-edge/L-XRF densitometry∗

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Precise measurement of uranium (U) and plutonium (Pu) concentrations is critical in spent nuclear fuel reprocessing for nuclear material accounting and process control. The hybrid L-edge/L-XRF densitometry (HLED), which combines the L-edge densitometry technique with the X-ray fluorescence (XRF) technique, can be applied to measure the concentration of U and Pu in both pure and mixed forms. In this study, a Geant4-based simulation model of the HLED system was established to optimize critical parameters including X-ray tube voltage, primary filter configuration, XRF detection angle, and collimator design. The simulation results reveal that the optimal parameters for the X-ray tube are an X-ray source voltage of 30 kV and a 0.15 mm Ni filter, with an XRF detection angle of 45°. An HLED platform was also developed on the basis of the simulation model for practical validation. The working curve was calibrated using standard uranium samples that spanned a concentration range of 14 to 162 g/L, producing a determination coefficient (R^2) of 0.999. Measurement validation showed relative errors of less than 2% and measurement precision of less than 0.5%. To address the low measurement precision for both low-concentration samples that produce weak L-edge absorption and high-concentration samples that exhibit strong L-edge absorption, an optimal path length and a current correction model of X-ray tube were presented, respectively. Furthermore, a uranium solution of 1.807 g/L and a thorium (Th) solution of 200 g/L were prepared to verify precision performance. The experimental results indicate that the measurement precision of the 1.807 g/L uranium solution can be improved from 2.356% to 1.588% by increasing the path length. An optimal path length of 11 mm for samples with a concentration below 10 g/L was obtained by simulation experiments. In addition, the precision of the 200 g/L thorium solution was increased by 35%, with the relative standard deviation decreasing from 2.35% to 1.588%.

Keywords: Hybrid L-edge/L-XRF densitometry, Spent nuclear fuel reprocessing, Uranium and plutonium concentrations, Measurement precision

Introduction

Accurate quantification of uranium (U) and plutonium (Pu) in spent nuclear fuel dissolver solutions is essential to maintain nuclear material accountancy during reprocessing operations, prevent special nuclear material (SNM) diversion, and enhance nuclear safety-security regimes [1, 2]. Standard nuclear material quantification methods employed in reprocessing facilities comprise isotope dilution mass spectrometry (IDMS), hybrid K-edge/K-XRF densitometry (HKED), constant-potential coulometry, potentiometric titration, laser fluorimetry, spectrophotometry, alpha spectrometry, and X-ray fluorescence spectroscopy [3]. Since the 1990s, HKED has been established as a standard industrial method for uranium/plutonium (U/Pu) quantification in 1AF and product streams of reprocessing facilities, enabling rapid analyses with sub-0.5% relative standard deviation precision [4].

The HKED from Canberra consists of a basic K-Edge densitometer (KED) with the additional capability for simultaneous X-ray fluorescence (XRF) analysis of induced X-rays. The typical configuration incorporates a constant potential X-ray system, two low-energy germanium (LEGe) detectors, standard NIM electronics and a computer for data acquisition, analysis and display [5]. Uranium concentration is quantified by KED through analysis of transmitted X-ray spectra across the U K-edge absorption threshold (115.590 keV), with concentration derived from transmission ratios measured across energy regions flanking the absorption edge. Concurrently, characteristic K-series emissions are detected by XRF to provide intensity measurements. Measurement precision achieves $<$ 0.5% for U at concentrations $>$ 50 g/L and $<$ 1.0% for Pu at concentrations $>$ 1 g/L. For mixed U/Pu matrices (U = 100 g/L; U/Pu ratio = 100:1), precision reached 0.1–0.2% for U and 0.7% for Pu [2–4]. Compared with the HKED, the HLED does not require heavy shielding to protect against K-series radiation of nuclear materials and a large power X-ray generation system because measuring the LIII-edge (17.167 keV) of uranium only needs a low-energy X-ray of below 50 keV. Therefore, the HLED equipment is portable and thus suitable for on-site measurement of nuclear materials [6].

Enhanced measurement precision for uranium/plutonium (U/Pu) quantification in spent nuclear fuel reprocessing is targeted by substantial research efforts. The inaugural KED prototype developed at the Karlsruhe Nuclear Research Center subsequently enabled the implementation of HKED. A supplementary 1 mm Cd filter is positioned adjacent to the X-ray tube, filtering both KED and XRF measurement beams. The tungsten shielding block between sample and KED detector contains a collimator aperture measuring 10 cm in length and 0.8 mm in diameter. The XRF detector is oriented at a 150° backward angle relative to the primary X-ray beam direction. The tungsten collimator preceding the XRF detector features a diameter of 2.5 mm and length of 10 cm. Ottmar found that the precision remains fairly constant at a level of about 0.22% for the uranium concentration range from about 150 to 300 g/L [1].

A 1 mm Cd primary filter is installed at the X-ray tube port in Xin' s HKED configuration, which reduced detector dead time. W-Ni-Fe alloy collimators are precision-machined to 10 cm length with apertures specified as 0.8 mm (KED) and 3.5 mm (XRF). Analytical precision is maintained at 0.24–0.31% for uranium standard solutions (150 to 300 g/L) [2]. The HKED system was upgraded through sample chamber reconstruction, X-ray tube replacement, and spectrum stabilization implementation for XRF measurements. Measurement reliability and analytical precision were enhanced by these modifications. For 1AF samples containing mixed U/Pu solutions (U:100–300 g/L, U/Pu 100), uranium measurement precision was measured at 0.1–0.2%, while plutonium precision was maintained below 0.7% [4]. An HKED system was developed by M. Bootharajan et al. for spent fuel reprocessing facilities. A relative error of $±$3% was observed through comparison between potentiometric titration and HKED measurements. For both uranium and plutonium, KED precision was maintained better than $±$0.9%, while XRF precision was constrained to < $±$1.6% (U) and < $±$0.8% (Pu) [7, 8].

The Monte Carlo method is regarded as a popular and effective approach for simulating and studying geometrical configuration effects on measurement precision [9–14]. Geant4 was employed by Song (Chengdu University of Technology) to optimize HLED structural configurations through analysis of X-ray tube, filters, collimators, and XRF detection angle. Using simulation data, an HLED test bench was constructed with two FAST SDD detectors. For aqueous U solutions (20–150 g/L), measurement precision less than 1.1% was achieved [15]. An HKED system model was developed with MCNP by Zhang et al. (East China University of Technology), with key parameters optimized including X-ray tube voltage, Fe filters for KED/XRF detectors, and collimator configurations. A comprehensive HKED measuring system was assembled using simulated structural characteristics, a COMET MXR-160 X-ray tube, and a GAMMA-X GMX HPGe detector. For U solutions at 50 g/L and 150 g/L, precisions of 0.56% and 0.19% were recorded, respectively [16, 17].

Global HLED research is founded upon HKED' s foundational technology. A portable LED system was developed by Los Alamos National Laboratory for uranium concentration measurement in reprocessing streams [18, 19]. In 2009, China' s first LED was developed by the China Academy of Atomic Energy Sciences (CAES), with an Amptek MINI-X silver-target X-ray tube excitation source and electrically cooled SDDs being utilized. Optimization of the spectral fitting region for uranium concentration measurements was performed using L-edge densitometry, resulting in a calibration curve covering 2–200 g/L U with measurement precision maintained below 0.5% [20]. Zr foils were employed as reference materials by Kang et al. to test L-edge densitometer stability. Through application of unified calibration curves, uranium measurement precision was maintained below 0.5% in both organic and aqueous phases at concentrations exceeding 10 g/L [21]. An L-edge densitometer was developed by Hong (Chengdu University of Technology) with digital signal processing and FAST SDD detectors, with relative errors of less than 4% being achieved for

U/Np/Pu measurements at 1–200 g/L concentrations. For samples exceeding 10 g/L concentration, measurement precision was maintained below 0.5% [22]. Lower measurement precision was reported at uranium concentrations approaching 2 g/L and 200 g/L in this research [23].

The development of an HLED prototype was pioneered by Seunghoon Park et al. through Geant4 modeling. The X-ray tube, sealed sample chamber, and dual silicon drift detectors (SDDs) were designated as core components. The X-ray tube was operated at 30 kV with a sample penetration depth of 2 mm; a 45° detection geometry was retained for XRF measurement [24–26]. In reference [27], it was demonstrated that high background intensity and short optical path lengths significantly impede transmission efficiency evaluation for low-concentration samples in LED systems.

Optimal measurement parameter configurations are required in system design to fulfill application demands, rendering parameter optimization critical. An HLED model is developed with Geant4 simulations to optimize crucial parameters including X-ray tube voltage, primary filter, XRF detection angle, and collimator design. The simulation-derived parameters were applied to construct an experimental platform. To address precision reduction at concentration extremes, extended optical paths were implemented for low-concentration samples and elevated tube current was employed for high-concentration samples, enhancing HLED measurement accuracy.

2.1. Measurement principles

L-edge absorption spectrometry determines elemental concentrations by detecting characteristic absorption discontinuities at element-specific L-edge energies in transmitted X-ray spectra. For incident photons of intensity $I_0(E)$ passing through a medium of thickness dx, the intensity attenuation dI(E) follows:

$$-dI(E) = I_0(E)\mu dx$$

where is the mass attenuation coefficient, = · , and is the density of the sample. Thus, Eq. (1) becomes:

$$-dI(E) = I_0(E)\mu_m \rho dx$$

Integrating Eq. (2) over sample thickness d gives:

$$I(E) = I_0(E)e^{-\mu_m \rho d}$$

The transmittance T of the rays after they pass through the sample can be expressed as:

$$\frac{I_0(E)}{I(E)} = e^{-\mu_m \rho d}$$

[Figure 1: see original paper] depicts the count rate versus incident photon energy for X-rays transmitted through a 40 g/L uranium solution and a 3 mol/L HNO_3 reference solution. A distinct absorption discontinuity occurs at the U LIII-edge. The shaded regions demonstrate regions of interest (ROI) flanking the absorption edge (ROI(E^-) 15.5–16.7 keV, ROI(E^+) 17.6–18.8 keV).

Within specific energy ranges, the mass attenuation coefficient follows:

$$\mu_m = a \cdot E^{-b}$$

where a and b are material-specific constants. Taking the natural logarithm of Eq. (4) yields:

$$\ln T = -aE^{-b}\rho d$$

Taking the logarithm again gives:

$$\ln[\ln(1/T)] = \ln(a\rho d) - b \ln E$$

Eq. (6) establishes a linear relationship between the double logarithm of the reciprocal of the transmittance and the logarithm of the energy value, as graphically demonstrated in [Figure 2: see original paper].

Two characteristic energies E^- (below LIII-edge) and E^+ (above LIII-edge) are selected flanking the LIII-edge. The transmittances of the incident ray at E^- and E^+ are respectively:

$$T(E^-) = e^{-[\mu_A(E^-)\rho_A + \mu_M(E^-)\rho_M]\cdot d}$$

$$T(E^+) = e^{-[\mu_A(E^+)\rho_A + \mu_M(E^+)\rho_M]\cdot d}$$

where and denote the mass attenuation coefficients for the analyte and matrix, respectively; and represent their corresponding concentrations. The transmittance ratio is then given by:

$$\frac{T(E^-)}{T(E^+)} = e^{(\Delta\mu_A\rho_A - \Delta\mu_M\rho_M)d}$$

included among these, Δ = (E^+) − (E^-), Δ = (E^-) − (E^+). Taking the natural logarithm of Eq. (9) and simplifying yields:

$$\ln T(E^-) - \ln T(E^+) = (\Delta\mu_A\rho_A - \Delta\mu_M\rho_M)d$$

The second right-hand side term denotes the matrix contribution, which includes all non-analyte elements in the sample. To eliminate matrix terms, the transmittance of the sample solution is normalized to that of a reference solution, resulting in analyte-specific transmittance. The reference solution employed in this paper is a 3 mol/L HNO_3 solution.

$$T'(E^-) = \frac{T(E^-)}{T_{ref}(E^-)}$$

$$T'(E^+) = \frac{T(E^+)}{T_{ref}(E^+)}$$

where T_{ref}(E^-) and T_{ref}(E^+) denote transmittance values measured at energies E^- and E^+ in the reference solution:

$$T_{ref}(E^-) = e^{-\mu_M(E^-)\rho_M \cdot d}$$

$$T_{ref}(E^+) = e^{-\mu_M(E^+)\rho_M \cdot d}$$

Matrix effects in the transmittance expression of Eq. (10) are eliminated by Eq. (13) and Eq. (14). Analyte concentration is calculated via:

$$\rho_A = \frac{\ln[T'(E^-)/T'(E^+)]}{\Delta\mu_A \cdot d}$$

In Eq. (15) the quantities , Δ and d are expressed in units ($g \cdot cm^{-3}$), ($cm^2 \cdot g^{-1}$) and [cm], respectively. To obtain the concentration in units of [g/L], Eq. (15) must be multiplied by a factor of 1000:

$$\rho_A = \frac{\ln[T'(E^-)/T'(E^+)] \cdot 1000}{\Delta\mu_A \cdot d}$$

To quantify U, characteristic energies $E^- = 16.7$ keV and $E^+ = 17.6$ keV flanking the LIII-edge are typically selected, where ln[T' (E^-)/T' (E^+)] quantifies the absorption edge jump magnitude. Δ represents the difference in mass attenuation coefficients, and d is the geometric thickness of the sample solution, equivalent to the optical path length for perpendicular X-ray incidence [1]. demonstrates the distinctive L-edge absorption energies and mass attenuation coefficient differences (Δ) for U, Th, and Pu.

In XRF measurements, for low-concentration samples, the element concentration can be directly determined by the peak area (intensity) of characteristic X-rays [28]. For mixed samples, the relative concentrations of elements can be determined by measuring the XRF spectrum and calculating the relative peak area ratio of the corresponding reference spectral lines. HLED quantifies U concentration using L-edge absorption (LED), while U/Pu concentration ratios are determined using characteristic peak intensity ratios (XRF), allowing Pu concentration to be calculated. The U/Pu concentration ratio can be calculated as follows:

$$\frac{U}{Pu} = \frac{A_U}{A_{Pu}} \cdot \frac{P_U}{P_{Pu}} \cdot \frac{ORE_{Pu}}{ORE_U} \cdot R_{U/Pu}$$

where A denotes atomic weight; P represents net characteristic X-ray peak intensity, and ORE is the relative detection efficiency, derived via linear interpolation of U L-line intensities (Lα, Lβ_1, Lβ_2) against known emission probabilities, which provides efficiency factors for uranium Lα_1 and plutonium Lα_1. The scaling factor, R_{U/Pu}, was empirically determined and represents the characteristic X-ray yield ratio between U and Pu under primary radiation excitation in mixed samples. The volumetric mass concentration of plutonium, _{Pu}, in mixed samples is calculated accordingly [29]:

$$\rho_{Pu} = \rho_U \times (U/Pu)^{-1}$$

2.2. Geometry optimization

The integrated hybrid L-edge/L-XRF system is composed of an X-ray tube, shields, a sample cell, and detectors. The schematic figure is shown as [Figure 3: see original paper]. HLED is formed by combining LED and XRF systems with a shared X-ray generator. X-rays from the tube are directed through a primary filter, where low-energy components are attenuated, resulting in background noise reduction and signal-to-noise ratio enhancement. Filtered X-rays are transmitted through the sample cell, interact with the solution and are absorbed. Collimated transmitted X-rays are acquired by the LED detector for transmission spectra generation, while scattering background interference is reduced by the collimator. During X-ray absorption, characteristic X-rays are emitted from the sample solution. XRF spectra are acquired through collection of collimated fluorescence photons at defined solid angles with an XRF detector. A co-axial geometry is employed in the LED measuring branch, with the X-ray tube, sample, and detector aligned collinearly. A defined tube-sample-detector angle is maintained in the XRF measuring branch to reduce scattering background within the spectral ROI [30].

Simulation samples included a 100 g/L uranium solution and a U-Pu mixed solution with a mass ratio of 100:1 (100 g/L U, 1 g/L Pu). As an example,

modeling a 100 g/L uranium sample in Geant4 yields a density of 1.20 g/cm^3, consisting of 91.67% HNO_3 and 8.33% uranium by mass.

(a) X-ray tube voltage

The intensity and energy distribution of the primary X-ray spectrum are influenced by the X-ray tube voltage. The excitation efficiency of sample elements is governed by this spectrum. Consequently, L-edge transmission and XRF measurement results will be affected [10]. The target solution is usually a feed solution containing uranium and plutonium, with the energy of L-edge of uranium and plutonium being 17.167 keV and 18.053 keV, respectively, and the X-ray continuous spectrum needs to cover the X-ray energy values of these edges. In Geant4 simulations, the primary photon energy range was configured to 20–50 keV, corresponding to a tube voltage range of 20–50 kV. The voltage dependence of L-edge transmission is illustrated in [Figure 4: see original paper]. It was found that the changes in L-edge transmission were small despite the significant changes in tube voltage. This was mainly due to the fact that the change in voltage intensity had a similar impact on the transmission rates T of the $T(E^-)$ and $T(E^+)$ energy levels on both sides of the L-edge. Consequently, tube voltage variations exert fewer effects on measured transmittance. Furthermore, L-edge transmittance calculations for U-Pu mixed solutions demonstrate minimal Pu spectral interference during uranium concentration quantification.

In XRF analysis, the peak-to-background (P/B) ratio is defined as characteristic peak intensity (P) divided by background intensity (B) [31]. Higher P/B ratios are correlated with enhanced statistical detection accuracy and reduced detection limits. The uranium Lα_1 (13.612 keV) and plutonium Lα_1 (14.276 keV) characteristic peaks are utilized for P/B ratio calculations. P/B ratios for uranium and plutonium Lα_1 characteristic peaks as functions of tube voltage are demonstrated in [Figure 5: see original paper].

An increase in characteristic P/B ratios for uranium and plutonium Lα_1 transitions with tube voltage is demonstrated in [Figure 5: see original paper]. This phenomenon is attributed to the primary X-ray continuum spectrum being the predominant source of XRF background. With increasing tube voltage, continuum intensity is enhanced, resulting in improved peak intensities concurrently with elevated spectral background levels. X-ray excitation requires incident energy exceeding the element' s absorption edge. Optimal excitation is achieved at energies slightly above this edge, which leads to the HLED system being operated at a 30 kV tube voltage.

(b) Primary filter

Characteristic X-rays of target elements are excited by primary radiation. Concurrently, bremsstrahlung continuum is generated, which elevates XRF background levels. X-ray filters need to be selected to achieve primary filtering of the X-rays to harden the spectrum while allowing for the instrument structure

within the range of tolerance. Three metallic filters (Fe, Ni, Cu) were simulated using Geant4, with the resultant L-edge transmission presented in [Figure 6: see original paper]. Limited L-edge transmission disparities among Fe, Ni, and Cu filters under 30 kV tube operation are indicated in [Figure 6: see original paper], which is due to the equivalent spectral filtering effects attributable to low-energy photon absorption. Consistent spectral filtering performance is provided by Ni filters, with exceptional radiation hardness and thermal stability maintained, establishing Ni as the optimal filter material for L-edge analysis.

Following Ni filter material selection, Ni filters spanning 0.05–0.25 mm thickness were modeled using Geant4, with P/B ratios for uranium and plutonium Lα_1 characteristic peaks calculated across thickness variations. The calculated results are displayed in [Figure 7: see original paper]. As shown in [Figure 7: see original paper], the P/B ratios for uranium and plutonium Lα_1 characteristic peaks show a dependence on filter thickness, reaching a maximum at a thickness of 0.15 mm Ni filter, with minima observed at 0.05 mm. Consequently, a 0.15 mm Ni filter was established as optimal.

(c) XRF detection angle

The detector-sample-tube angle ( ) in the XRF measuring branch was simulated across a 15°–90° range, with results presented in [Figure 8: see original paper]. P/B ratios were calculated for the uranium and plutonium Lα_1 characteristic peaks. A decline in P/B ratios with increasing detector-sample-tube angle is demonstrated in [Figure 8: see original paper], with maximum values attained at = 15°.

Higher P/B ratios for uranium and plutonium Lα_1 peaks at small angles compared to large angles are revealed by Geant4 simulations. However, a 45° detection angle was selected as the operational angle in practical HLED configurations. This choice balances the need for optimal signal-to-noise with instrumental constraints, such as physical space for detector and tube shielding. Consequently, for all subsequent simulations, the detector-sample-tube angle in the XRF measuring branch was fixed at 45°.

(d) Collimator design

Collimators must be incorporated in the incident optical path to reduce measurement interference from scattered photons and block off-axis X-rays. The impact of incident collimator diameter on measurement outcomes was simulated using Geant4, employing Cu collimators with diameters ranging from 1 to 3 mm and a fixed length of 100 mm. Simulated L-edge transmission versus incident collimator diameter are demonstrated in [Figure 9: see original paper]. Minimal variation in L-edge transmission across collimator diameters is illustrated in [Figure 9: see original paper]. This stability is attributed to diameter fluctuations exerting similar effects on E^- and E^+ of L-edge transmission. When collimator diameter matches the X-ray tube exit window dimensions, the inci-

dent photon flux is maintained nearly constant. The P/B ratios for the uranium and plutonium Lα_1 characteristic peaks as functions of collimator diameter are displayed in [Figure 10: see original paper]. An increase in collimator diameter is illustrated in [Figure 10: see original paper] to induce a monotonic rise in P/B ratio of uranium Lα_1, whereas P/B ratio of plutonium Lα_1 exhibits initial increase followed by saturation. In practical HLED systems, incident collimator diameters should be minimized subject to operational constraints. Overly narrow dimensions are revealed by simulations to reduce incident photon flux, causing insufficient detector counts. To mitigate statistical fluctuation effects, diameters should be progressively enlarged to enhance photon flux; however, excessive enlargement is rendered ineffective when approaching X-ray tube exit window dimensions.

Based on these findings, the impact of incident collimator length on L-edge transmission was simulated using Geant4 across a 5–10 cm range, with optimization results presented in [Figure 11: see original paper]. Small changes in L-edge transmission with increasing collimator length were indicated in [Figure 11: see original paper]. Scattered photons are effectively attenuated by longer collimators, reducing intensity in transmission spectra. Similar reductions in both T(E^-) and T(E^+) intensities result. P/B ratios of uranium and plutonium Lα_1 characteristic peaks versus collimator length are demonstrated in [Figure 12: see original paper]. An inverse relationship between P/B ratios and incident collimator length is demonstrated in [Figure 12: see original paper]. Background contributions to measurements are suppressed by moderately increasing collimator length in practical applications. However, simulation environments are characterized by lower particle counts than experimental conditions, and excessive collimator length will introduce statistical fluctuation effects. Simulated trends of P/B ratios versus collimator diameter and length parameters are presented, establishing theoretical foundations for collimator optimization in HLED devices.

3. Experimental device

Key HLED parameters were simulated utilizing Geant4. Optimal configurations were established, including a tube voltage of 30 kV, a 0.15 mm Ni filter, an XRF detection angle of 45°, and scenario-dependent collimator adjustments. An HLED device was constructed using these parameters for experimental validation of simulation predictions.

The X-ray tube functions as the HLED radiation source, with controlled primary X-rays generated to excite characteristic emissions from samples. Low-power X-ray tubes are applicable owing to the target element' s L-absorption limit and low-energy L-series emissions (<20 keV). The KYW2000A-type X-ray tube was selected for the experimental platform, featuring: rated voltage of 50 kV, rated current of 1 mA, maximum output power of 50 W, beryllium window thickness of 200 µm, tungsten anode target, and air-cooled heat dissipation.

The HLED system is equipped with two dedicated detectors: one dedicated to transmission spectroscopy (LED) and another to X-ray fluorescence spectroscopy (XRF). Two XR-100-type FAST SDD detectors manufactured by AMETEK are employed in the experimental platform. The detectors feature an active area of 25 mm^2, 500 µm depletion depth, and 12.5 µm beryllium window. Energy resolution is specified as 125 eV FWHM at 5.9 keV, with a peak-to-background ratio of 26,000:1 (typical) and thermoelectric cooling.

The configured HLED experimental platform is presented in [Figure 13: see original paper]. Two irradiation modes, short optical path length and long optical path length, are achieved through distinct sample cell placement methods combined with a metal sample holder, enabling selectable transmission paths.

Uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) reagent and 3 mol/L HNO_3 solution were employed to prepare aqueous uranium standards at varying concentrations. Precise masses of $UO_2(NO_3)_2 \cdot 6H_2O$ were calculated, weighed, dissolved in 3 mol/L HNO_3, and quantitatively transferred to 10 mL volumetric flasks to achieve target uranium concentrations. Final uranium concentrations were verified by inductively coupled plasma optical emission spectrometry (ICP-OES). Aqueous uranium standards were prepared at seven concentrations: 14.235, 31.469, 48.637, 71.778, 100.233, 124.480, and 162.144 g/L. The representative sample (U-124.480 g/L) was modeled in Geant4. Comparative analysis of simulated and experimental spectra is presented in [Figure 14: see original paper] with normalized ordinate values. Clearly visible uranium L-edge features appear in both simulated and experimental transmission spectra, with high agreement in edge jump magnitudes. Higher counts in the high-energy region (>20 keV) of the simulated spectra, compared to experimental results, are attributed to differences in the reference spectra used or the inherent background characteristics. Precise alignment among three uranium characteristic peaks ($L\alpha_1$, $L\beta_1$, $L\beta_2$) is exhibited in the XRF spectra for both simulations and experiments. Experimentally, the enhanced detection of scattered photons increases background intensity in experimental spectra relative to simulations.

Aqueous uranium standards at specified concentrations were measured experimentally under a 30 kV tube voltage and a 39.2 µA tube current. Six replicate 300-second measurements per sample were averaged to establish the uranium calibration curve presented in [Figure 15: see original paper]. The linear fitting of $\ln[T'(E^-)/T'(E^+)]$ and U concentration showed a coefficient of determination (R^2) of 0.999. Measured transmittance values at each concentration were input into the calibration curve to calculate derived U concentrations. The results between calculated and nominal U concentrations are tabulated in . Precision was evaluated by calculating the relative standard deviation (RSD) from six replicate measurements. As shown in , aqueous uranium samples (14.235–162.144 g/L) exhibit relative errors of less than 2% and RSDs of less than 0.5%.

Geant4 simulations of key HLED parameters—including tube voltage, primary filter, XRF detection angle, and collimator configurations—are presented in this section. Design standards for the HLED experimental platform are established

by these optimized parameters. Both qualitative and quantitative analyses of uranium samples are enabled by the implemented platform.

4. Precision enhancement in extreme concentration analysis

4.1. Experiments for low-concentration sample

The background radiation and the short optical path length can affect the transmission of low-concentration samples. During spectroscopic analysis of a 1.8 g/L aqueous uranium sample, the L-edge absorption features in transmission spectra were significantly diminished, making them barely discernible. Per the LED measurement principle (Eq. (15)), reduced ln[T' (E^-)/T' (E^+)] values are obtained at lower sample concentrations when the optical path length d is fixed. For low-concentration samples, increased optical path length enhances X-ray attenuation through the solution, producing larger L-edge jump magnitudes in transmission spectra. Consequently, the impact of statistical fluctuations is reduced, thereby improving measurement precision.

Transmission spectra of 1.8 g/L uranium samples under short and long optical path lengths are compared in [Figure 16: see original paper]. The entire energy spectrum count rate is reduced by increased X-ray transmission thickness. The vertical axis is normalized to facilitate comparative observation. Increased depth of the absorption edge region is observed under long optical path lengths, as shown in [Figure 16: see original paper]. Four low-concentration uranium samples were measured under both short and long optical path lengths. Measurements were conducted at 30 kV tube voltage and 39.2 μA tube current, with six 300-second repeats per sample averaged. Two calibration curves were developed using four low-concentration uranium samples. Derived uranium concentrations were computed by applying the calibration curves to measured transmission spectra at each concentration. Resultant precisions are presented in .

Reduced measurement RSD is indicated in for low-concentration samples employing longer optical path lengths. These findings reveal that long optical paths improve measurement precision for low-concentration samples in practical analytical applications.

Transmission spectra were generated by Geant4 simulations for four uranium samples across 5–20 mm path lengths, yielding sixteen calibration curves correlating transmittance with uranium content. Uranium concentrations were computed by entering simulated ln[T' (E^-)/T' (E^+)] values at varying optical path lengths into corresponding calibration curves. Relative errors were calculated through comparison with nominal concentrations, with results illustrated in [Figure 17: see original paper].

Minimization of relative errors across four low-concentration uranium samples at an 11 mm optical path length is demonstrated in [Figure 17: see original paper].

That 11 mm is established as the ideal optical path length for low-concentration uranium samples in LED transmission analyses is shown by simulation results, confirming that measurement precision for low-concentration specimens is enhanced by increased optical path length.

4.2. Experiments for high-concentration sample

Measurement precision is found to decline in HKED studies when uranium concentrations exceed a threshold value [3]. During HLED measurements of high-concentration uranium solutions near the upper detection limit, intense X-ray attenuation results in severe count rate reduction across the L-edge region, where statistical fluctuations become the dominant factor limiting measurement precision. Differentiating the densitometry Eq. (15) for the ratio of transmissions $T(E^-)/T(E^+) = R$ yields for the uncertainty of the uranium concentration:

$$\frac{\Delta\rho}{\rho} = \frac{1}{\Delta\mu \cdot \rho \cdot d} \cdot \frac{\Delta R}{R}$$

The uncertainty ΔR in Eq. (19) is determined by counting statistics and the transmittance ratio computation methodology. When consistent computation methods are applied with negligible counting error variation, ΔR is maintained approximately constant. Within a defined concentration range, measurement precision is enhanced by increasing sample concentration ( ). However, strong X-ray attenuation in high-concentration samples causes large counting errors and an increased ΔR, which significantly degrades measurement precision.

The intensity of the X-ray flux is altered by increasing the X-ray tube current. Consequently, for high-concentration samples, the L-edge count rate is increased by elevated tube current, reducing the statistical fluctuation effect and improving measurement precision.

Reference and sample transmission spectra are typically acquired under identical tube current conditions. However, constantly increasing current induces reference spectrum count rate reduction through detector dead time effects, potentially causing count rate saturation that disrupts spectral acquisition. Therefore, measurement integrity is optimized by selectively increasing current for sample spectra while maintaining reference spectrum current. When tube currents differ between reference and sample spectra, current corrections must be implemented prior to spectral normalization [2]. The relationship between reference and sample spectrum count rates under differing tube currents is described by:

$$\left(\frac{N_R}{N_S}\right)_{corrected} = \alpha \cdot \left(\frac{N_R}{N_S}\right)_{measured}$$

where N_R and N_S denote the counts of reference and sample transmission spectra, α represents the correction factor defined by:

$$\alpha = \ln \frac{I_S \cdot P_S \cdot t_S}{I_R \cdot P_R \cdot t_R}$$

where I_S and I_R denote tube currents for sample and reference spectra, with I_R = 39.2 μA and I_S = 78.4 μA; P_S and P_R represent detector efficiencies, typically P_S/P_R 1. t_S and t_R are measurement durations with t_S/t_R = 1. Eq. (20) then simplifies to:

$$\alpha = \ln \frac{I_S}{I_R}$$

Substituting Eq. (21) into Eq. (19) yields:

$$\left(\frac{N_R}{N_S}\right)_{corrected} = \ln \frac{I_S}{I_R} \cdot \left(\frac{N_R}{N_S}\right)_{measured}$$

Spectral correction is performed using Eq. (22) when tube currents differ between sample and reference spectra. A 200 g/L aqueous thorium solution was prepared for high-concentration experiments due to limited availability of uranium standards. The relationship between ln[ln(1/T)] and ln(E) across the LIII-edge under varying tube currents is illustrated in [Figure 18: see original paper]. The dependency of ln[ln(1/T)] on ln(E) under increasing tube current is demonstrated in [Figure 18: see original paper]. Following tube current increase, fitting coefficients flanking the L-absorption boundary were elevated. Enhanced count rates across the full spectrum resulted in smoothed spectral curves, indicating reduced statistical fluctuation effects.

Spectroscopic measurements were conducted on a 200 g/L thorium solution. The sample measurement tube current was incrementally elevated from 39.2 to 548.8 μA, while the reference spectrum tube current was maintained at 39.2 μA. Six replicate 300-second measurements were acquired per tube current setting at 30 kV tube voltage. RSD results calculated via ln[T(E^-)/T(E^+)] for the high-concentration thorium specimen are presented in [Figure 19: see original paper]. Improved measurement precision for a 200 g/L thorium solution with increasing tube current is demonstrated in [Figure 19: see original paper], achieving RSD values below 0.5%. For high-concentration solutions, reference and sample spectra must be optimized through differential tube currents, as demonstrated by these findings. Experimentally, selective elevation of sample spectrum tube current increases L-edge count rates, enhancing precision for high-concentration specimens.

5. Conclusion

A Monte Carlo model for the HLED measurement system was developed in this study. The X-ray tube was operated at the optimized voltage of 30 kV,

with an XRF detection angle of 45° being determined through systematic optimization. A 0.15 mm Ni filter is implemented, and collimator dimensions are configured as field-adjustable per experimental requirements. The HLED experimental platform was constructed using simulation-optimized settings. Calibration curves were established for aqueous uranium samples (14.235–162.144 g/L), demonstrating a coefficient of determination (R^2) of 0.999. Relative errors were maintained below 2%, while measurement precision was constrained to <0.5% across the concentration range during validation. To address low measurement precision in low-concentration samples exhibiting weak L-edge absorption and high-concentration samples demonstrating strong L-edge absorption, an optimal path length and an X-ray tube current correction model are respectively presented.

For low-concentration uranium analysis (1.807 g/L), optical path length augmentation resulted in RSD reduction from 2.356% to 1.588%; for high-concentration thorium analysis (200 g/L), tube current elevation led to RSD reduction from 2.760% to 0.408%, indicating enhanced measurement precision.

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Note: Figure translations are in progress. See original paper for figures.