

Overcoming the sensitivity–selectivity trade-off in laser-induced breakdown spectroscopy (LIBS) for uranium isotope analysis via joint spectral decomposition of single- and double-pulse spectra

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ABSTRACT

Reliable analysis of uranium isotopes (^{235}U and ^{238}U) is essential throughout the nuclear fuel cycle. Laser-induced breakdown spectroscopy (LIBS) has emerged as a promising technique for rapid detection of uranium. However, its application to isotope analysis is hindered by a fundamental sensitivity-selectivity trade-off: High-energy laser pulses, while essential for enhancing sensitivity, exacerbate the overlap between closely spaced spectral features, thereby reducing isotope selectivity. To circumvent this dilemma, the present study proposes a joint spectral decomposition framework that integrates two complementary spectra obtained using single-pulse (SP) and double-pulse (DP) LIBS. SP spectra preserve the narrow spectral features required for isotope discrimination, whereas DP spectra provide enhanced emission intensity and detection sensitivity. By simultaneously fitting the SP and DP spectra under a shared isotope-ratio constraint, the proposed framework combines DP-enhanced sensitivity with SP-derived isotope selectivity, achieving a uranium limit of detection (LOD) of 0.008% in a soil matrix while keeping the isotope-quantification bias within approximately 1 percentage point. These results demonstrate the feasibility of the proposed framework for improving the analytical performance of LIBS-based uranium isotope analysis and provide a basis for further validation toward rapid uranium isotope screening.

1. Introduction

Accurate characterization of uranium-bearing materials plays a critical role in the nuclear fuel cycle, including uranium processing, fuel fabrication, safeguards verification, environmental monitoring, and nuclear forensic analysis [1–3]. In particular, the isotopic abundance of ^{235}U and ^{238}U is fundamental to distinguishing materials intended for peaceful energy production from those that may indicate potential weaponization pathways [4]. Therefore, uranium isotope analysis is required for various conditions, including rapid screening of environmental samples, process residues, contaminated materials, and other complex matrices encountered in nuclear safeguards and security.

Traditionally, uranium isotopes have been analyzed using mass spectrometry and radiation detection techniques [5–9]. Mass spectrometry provides exceptional sensitivity, precision, and isotopic resolution, and radiation-based measurements offer nondestructive means of

estimating uranium enrichment. Despite the high performance of these techniques, their application for rapid, direct, and in situ analysis is often limited by intensive sample preparation, lengthy acquisition times, and a reliance on specialized laboratory instrumentation. These practical bottlenecks underscore the need for complementary analytical methods capable of prompt screening with minimal sample handling to provide actionable data prior to confirmatory analysis.

In this context, laser-induced breakdown spectroscopy (LIBS) offers an attractive alternative, as it enables direct elemental analysis with minimal to no sample preparation [10]. The process involves a focused pulsed laser that ablates minute quantities of material, generating a laser-induced plasma at the sample surface [11]. In this plasma plume, excited atoms and ions release their characteristic emission, which enables direct elemental analysis without the need for time-consuming preparation [12]. Moreover, because both the excitation laser and the emitted light can be transmitted over distance, LIBS can be configured

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for remote detection, substantially reducing the risks associated with the direct handling of radioactive or contaminated materials [12]. Accordingly, LIBS has been extensively explored for uranium detection in diverse matrices, including soils, glasses, and fuel-related materials [13–16].

While LIBS has proven effective for these elemental analyses, further enhancing its detection sensitivity, particularly for trace-level uranium, generally necessitates greater energy deposition [17]. To this end, double-pulse (DP) LIBS has been extensively studied as a strategy to boost emission intensity and lower detection limits [17–19]. In a typical DP configuration, two laser pulses are delivered with a precisely controlled temporal delay [18]. The first pulse initiates the ablation to form an initial plasma plume, while the second pulse deposits additional energy into this evolving plume [19]. This subsequent energy injection reheats the plasma and further excites the ablated species, resulting in a more intense and longer-lasting emission. Consequently, the DP configuration can significantly improve the signal-to-background ratio and lower the elemental detection limit by orders of magnitude relative to conventional single-pulse (SP) LIBS [20].

While these advantages significantly benefit elemental detection, DP-LIBS has seen limited application in quantitative analysis of uranium isotopes due to concerns over isotopic selectivity. Unlike elemental identification, isotopic analysis demands the precise discrimination of ^{235}U and ^{238}U contributions within a single spectral feature. This task is inherently difficult because isotopic differences induce only a minute displacement in emission wavelength (*i.e.*, isotope shift), which for uranium is typically only several picometers [13]. Since this shift is often comparable to or smaller than the spectrometer resolution, the emissions from ^{235}U and ^{238}U typically merge into a single, overlapped spectral profile.

To extract isotope-specific information from such unresolved profiles, spectral decomposition has been employed [15]. In this approach, the observed feature is modeled as the summation of two line-shape functions, most commonly Lorentzian profiles, with the isotopic composition estimated from their relative areas [16]. However, the reliability of this decomposition hinges on a delicate balance between two competing factors: emission intensity (sensitivity) and spectral linewidth (selectivity). Although DP-LIBS substantially boosts intensity, the associated increase in plasma temperature and electron density can trigger enhanced spectral line broadening [17]. Given that the uranium isotope shift is so minimal, even moderate broadening significantly increases the spectral overlap between the isotopes. This creates a fundamental tension where DP-LIBS offers superior sensitivity but inferior selectivity, whereas SP-LIBS preserves narrower profiles at the expense of signal strength.

To resolve this sensitivity–selectivity trade-off, we introduce a joint spectral decomposition framework that couples SP- and DP-LIBS observations as complementary datasets for uranium isotope analysis. Rather than analyzing the spectra independently, the proposed method performs a simultaneous fit to the paired SP and DP spectra, which are bridged by enforcing a shared isotope ratio during optimization. In this integrated approach, the narrow SP spectrum provides the essential isotopic discrimination to constrain the spectral structure, while the enhanced signal intensity of the DP spectrum stabilizes the quantification at trace concentrations. By coupling these complementary datasets into a single physically constrained solution, the proposed methodology effectively mitigates the sensitivity–selectivity conflict. This strategy provides a robust and practical basis for rapid uranium isotope screening, offering a powerful analytical capability for nuclear safeguards, environmental monitoring, and nuclear security.

2. Experimental

2.1. Optical configuration

The experimental setup for both single- and double-pulse LIBS is

illustrated in Fig. 1. To enhance uranium emission through sequential laser-plasma interaction, a double-pulse configuration utilizing 2 ns Nd:YAG lasers (Continuum, Surelite, 20 Hz) was employed. The initial plasma was generated by a 266 nm laser pulse focused onto the sample surface, followed by the introduction of a 1064 nm laser pulse to reheat the evolving plasma plume after a controlled inter-pulse delay. Synchronization of the laser pulses was managed via digital delay generators (Stanford Research Systems, DG535). To acquire complementary single-pulse spectra, the 1064 nm laser path was blocked, ensuring that detection conditions remained identical between the SP and DP measurements.

The selection of pulse energies and timing parameters was guided by a systematic optimization of the DP configuration [21]. The ablation and reheating pulse energies were set to 40 mJ and 120 mJ, respectively, with an inter-pulse delay of 3 μs , which provided optimized uranium emission and stable spectral acquisition. The resulting plasma emission was collected via fiber optics and routed to a Czerny–Turner spectrometer (Andor Technology) coupled with an intensified charge-coupled device (ICCD) operating with a gate delay of 1 μs and a gate width of 30 μs . A 2400 grooves/mm grating and a 60 μm entrance slit were used, providing a spectral dispersion of approximately 3 p.m./pixel. Wavelength calibration was performed before each measurement using a uranium hollow-cathode lamp, from which the instrumental FWHM was determined to be approximately 12 p.m. The approximately 25 p.m. isotope shift is therefore greater than twice the instrumental FWHM, providing sufficient resolution for the constrained spectral decomposition employed in this study.

All experiments were conducted within a shielded chamber containing atmospheric air, utilizing optical ports for laser delivery and photon collection. Each recorded spectrum represents an accumulation of 100 laser shots for the SP configuration, or 100 sequential shot pairs for the DP configuration.

2.2. Sample preparation

Because material composition and impurities can influence plasma behavior and measurement reliability in plasma-based experiments [22, 23], well-characterized certified reference materials were employed in this study. Uranium-doped soil samples were prepared using uranium oxide (U_3O_8) from certified reference material (CRM U200). This material was selected because its nominal ^{235}U abundance of 20% lies near the conventional enrichment threshold that distinguishes low-enriched uranium (LEU) from highly enriched uranium (HEU) [24]. The uranium oxide was precisely weighed and mechanically blended with soil powders (NIST SRM 2710a) to ensure homogeneity. A sample series was generated with total uranium concentrations of 0.3, 1, 3, 5, and 10 wt%. The blended powders were then pressed into solid pellets with a diameter of approximately 10 mm. To mitigate the effects of localized sample heterogeneity and prevent severe cratering from repeated laser ablation, the sample pellets were mounted on a rotating stage during spectral acquisition. For each concentration level, five replicate pellets were prepared and analyzed to assess reproducibility and quantify measurement uncertainty.

3. Results and discussion

3.1. Spectral features of uranium isotopes from single- and double-pulse configurations

As a foundational step toward uranium isotope analysis, we first compared representative spectra obtained using the single-pulse (SP) and double-pulse (DP) LIBS configurations. Because uranium has a complex electronic structure, laser-induced plasma produces numerous emission lines, making careful line selection essential for isotope analysis [13]. The U II line at 424.4 nm was selected as the primary analytical feature because of its relatively pronounced isotope shift of

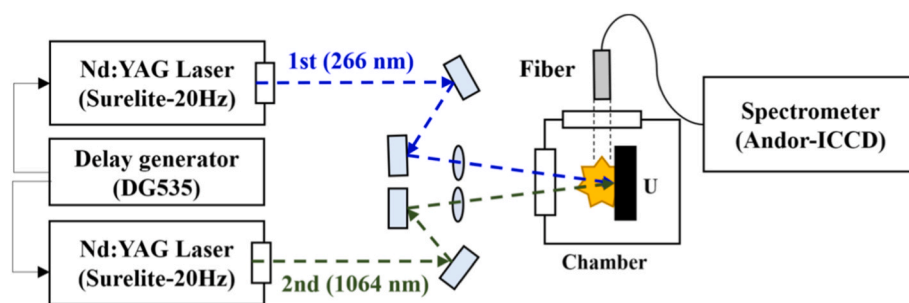


Fig. 1. Schematic diagram for double-pulse laser-induced breakdown spectroscopy.

approximately 25 p.m. between ^{235}U and ^{238}U [15]. Fig. 2a presents the corresponding spectra for the SP (black) and DP (red) configurations. The DP configuration produced a substantially stronger emission signal, consistent with plasma reheating and further excitation induced by the second laser pulse [19].

The practical improvement in uranium detection was further quantified by determining the limit of detection (LOD) in soil samples. Fig. 2b plots the emission intensity as a function of total uranium concentration for both configurations. Although both approaches exhibited strong linearity, confirming their applicability to elemental quantification in complex soil matrices, the DP calibration curve displayed a markedly steeper slope, reflecting its greater sensitivity. Based on the standard 3σ criterion [20] using the calibration curves shown in Fig. 2b, the elemental uranium LOD was calculated according to $\text{LOD} = 3\sigma/m$, where σ represents the standard deviation of the analytical signal obtained from five independently measured blank soil samples, and m is the slope of the corresponding calibration curve. Based on this procedure, the DP configuration yielded an estimated elemental uranium LOD of approximately 0.008 wt%. This value represents a 15-fold improvement over the corresponding SP-LIBS elemental LOD of 0.12 wt% and is much lower than previously reported LIBS detection limits for the U II 424.4 nm feature in soil [15]. These results demonstrate the effectiveness of DP-LIBS for extending elemental detection to trace concentrations.

However, the sensitivity enhancement does not necessarily translate into improved isotope analysis, for which sufficient spectral discrimination is equally critical. The SP spectrum exhibits relatively low emission intensity but retains discernible spectral features associated with the ^{235}U and ^{238}U components, thereby providing the selectivity required for spectral decomposition. In contrast, the DP spectrum provides substantially enhanced intensity but undergoes pronounced line broadening because of Doppler and Stark effects from elevated electron density and temperature [25]. This spectral broadening increases the

overlap between isotope-specific features, reducing isotope selectivity. These contrasting characteristics establish a fundamental analytical trade-off: SP-LIBS favors isotopic selectivity at the expense of sensitivity, whereas DP-LIBS favors sensitivity at the expense of isotopic selectivity. Because neither configuration alone simultaneously provides both capabilities, it is necessary to evaluate how these contrasting spectral characteristics impact the performance of isotope quantification, as detailed in the following section.

3.2. Spectral decomposition and sensitivity-selectivity trade-off

The contrasting spectral characteristics of the SP and DP configurations are expected to influence not only the observed spectral profiles but also the analytical performance of isotope quantification. To assess this effect, the $^{235}\text{U}/^{238}\text{U}$ ratio was quantitatively estimated from each spectrum. Because the isotope-specific components of the U II 424.4 nm line are not fully resolved, the measured emission profile must be decomposed into the ^{235}U and ^{238}U components. Accordingly, spectral decomposition based on Lorentzian fitting was employed [15]. Although Doppler broadening can introduce Gaussian contributions to the measured line profile, the observed LIBS profiles were considered to be dominated by the Lorentzian contribution associated primarily with Stark broadening. Introducing a Voigt profile would require additional fitting parameters to separately account for the Gaussian and Lorentzian contributions, which may increase parameter covariance and fitting uncertainty given the strong overlap between the ^{235}U and ^{238}U components. Consistent with this practical consideration, Lorentzian functions have commonly been employed for spectral decomposition of the U II 424.4 nm isotope feature in previous studies [15,16]. Therefore, the Lorentzian model was adopted for the present analysis. The measured spectral intensity, I^{exp} , was modeled as follows:

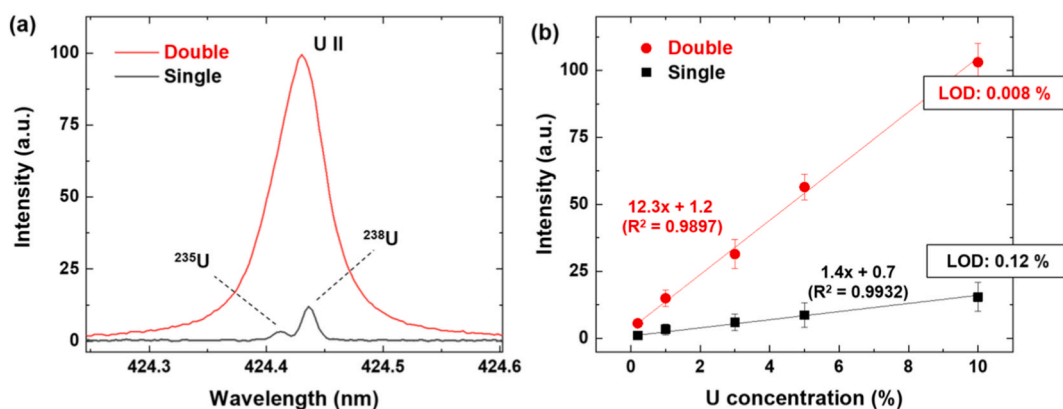


Fig. 2. (a) Representative single-pulse and double-pulse LIBS spectra around the U II emission feature at 424.4 nm. (b) Calibration with emission intensity as a function of uranium concentration for single-pulse and double-pulse measurements. The double-pulse configuration provides a stronger uranium emission signal and lowers the limit of detection (LOD) from 0.12% to 0.008% total U.

$$I^{exp}(\lambda) = [L(\lambda_{235}, w_{235}) \times R + L(\lambda_{238}, w_{238}) \times (1 - R)] \times A + C + \varepsilon(\lambda) \quad \text{Eq. (1)}$$

The Lorentzian function, $L(\lambda, w)$ [16], is defined with center wavelengths (λ_{235} and λ_{238}) and the linewidths (w_{235} and w_{238}). A represents a peak area, and C denotes the constant background. The term $\varepsilon(\lambda)$ signifies the fitting residual. The isotopic ratio (R) is determined as the relative fraction of ^{235}U within the total uranium:

$$R = \frac{U_{235}}{U_{235} + U_{238}} \quad \text{Eq. (2)}$$

To reliably extract the isotope ratio R while minimizing the residual $\varepsilon(\lambda)$, physically informed constraints were incorporated into the fitting model. These constraints reduce parameter covariance and limit the number of free variables while preserving the known physical characteristics of the transition. First, even though the center positions (λ_{235} and λ_{238}) may fluctuate due to plasma-induced wavelength shifts, the fundamental isotope shift between the ^{235}U and ^{238}U components remains rigidly constant for a given transition [15]. Therefore, the center wavelength of the ^{238}U component (λ_{238}) was strictly tied to that of the ^{235}U component (λ_{235}) using this fixed isotope shift, leaving only a single wavelength parameter to be optimized. Second, the ^{235}U and ^{238}U components were constrained to share a common linewidth (w). Because both components originate from the same electronic transition and experience the same plasma environment, isotope-dependent differences in line broadening are expected to be negligible. In addition, the hyperfine structure of the ^{235}U component was assumed to be negligible in this transition [16]. With these constraints, each experimental spectrum was described by five independent fitting parameters, expressed as $\theta = \{A, \lambda, w, C, \text{ and } R\}$.

All spectral fitting was performed in Python 3.11 using the trust-region reflective algorithm implemented in SciPy for bound-constrained nonlinear least-squares optimization. The initial amplitudes of the ^{238}U and ^{235}U components were estimated from the measured peak intensity, and the background term was initialized from the mean signal intensity in a line-free spectral region. The relative center wavelengths of the two isotope components were constrained using the fixed isotope shift of 0.025 nm. The fitted linewidth was constrained to be no smaller than 0.012 nm, corresponding to the instrumental spectral resolution. Optimization was terminated when the change in the objective function or fitted parameters, or the gradient norm, satisfied a tolerance of 10^{-8} , with a maximum of 1000 function evaluations. To assess the robustness of the joint fitting with respect to initialization, the optimization was repeated using combinations of initial isotope abundance, center wavelength, and linewidth values.

Across all tested initial conditions, the fitted ^{235}U abundance varied by less than 0.02 percentage points, indicating stable convergence to a consistent solution over the tested initialization range.

Using this model, spectral decomposition was first performed independently for the SP and DP spectra. Fig. 3 presents representative fitting results for a sample containing 10% total uranium with a nominal ^{235}U abundance of 20%. As shown in Fig. 3a, the SP spectrum exhibits a relatively narrow spectral profile, preserving the shoulder associated with the minor ^{235}U component and the dominant contribution from ^{238}U . This isotope-sensitive structure enables the two overlapping components to be separated with greater selectivity. The independent fitting of the SP spectrum yielded a ^{235}U abundance of 19.1% with a standard deviation of 1.1%, corresponding to an absolute bias of only 0.9 percentage points relative to the nominal value.

In contrast, although the DP configuration produces a substantially stronger U II emission signal, the resulting spectral profile is considerably broader (Fig. 3b). The increased linewidth enhances the overlap between the ^{235}U and ^{238}U components and obscures the subtle spectral structure. Under these conditions, the fitting algorithm exhibits greater variability in partitioning the integrated area between the two overlapping components, increasing the uncertainty in the estimated isotope ratio. Consequently, isotope quantification based on the DP spectrum yielded a ^{235}U abundance of 23.3% with a standard deviation of 3.4%, corresponding to an absolute bias of 3.3 percentage points. These results demonstrate that the enhanced sensitivity provided by DP-LIBS does not necessarily translate into improved isotope-ratio quantification. Despite its lower emission intensity, the narrower SP spectrum retains greater isotope-specific information and therefore produces a more accurate and precise estimate.

The isotope-ratio quantification was further evaluated depending on total uranium concentration, using the average absolute bias and standard deviation of the estimated ^{235}U abundance (Fig. 4). The absolute bias was calculated relative to the nominal ^{235}U abundance, while the standard deviation was determined from the variation among five replicate measurements. Accordingly, a lower absolute bias indicates greater accuracy, whereas a lower standard deviation indicates greater precision. Fig. 4a summarizes the results obtained from the spectral decomposition of the SP spectra. At relatively high uranium concentrations, SP-LIBS provided low bias and standard deviation because its narrower spectral profile preserved sufficient separability between the ^{235}U and ^{238}U components. However, as the uranium concentration decreased, both bias and deviation increased substantially. The average bias was 0.9 percentage points at 10% U, but increased to 7.2 percentage points at 0.3% U, accompanied by a pronounced increase in standard

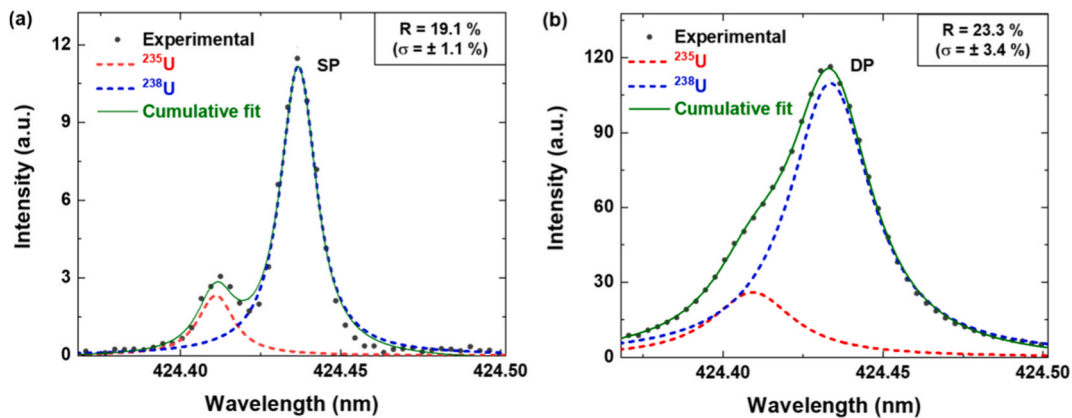


Fig. 3. Representative spectral decomposition of (a) single-pulse and (b) double-pulse spectra for uranium-doped soil samples containing 10% total uranium with a nominal ^{235}U abundance of 20%. Black dots show the experimental spectrum. In spectral decomposition using Lorentzian profiles, red, blue, and green curves indicate the ^{235}U component, ^{238}U component, and cumulative fit, respectively. (a) The SP spectrum provides a sharper spectral profile and yields an estimated ^{235}U abundance (R) of 19.1% with a standard deviation of 1.1%. (b) The DP spectrum exhibits a broader spectral profile and stronger overlap between the ^{235}U and ^{238}U components, resulting in an estimated ^{235}U abundance (R) of 23.3% with a standard deviation of 3.4%.

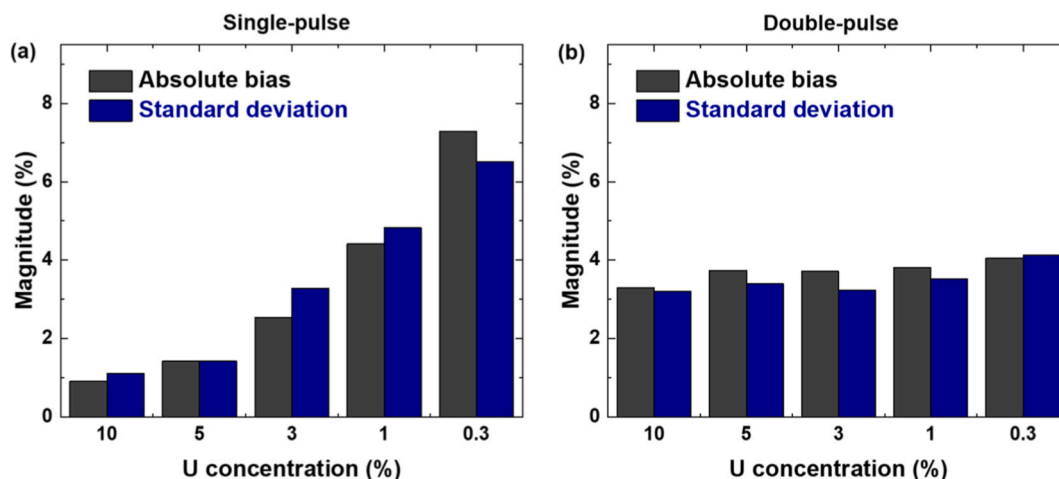


Fig. 4. Concentration dependence of uranium isotope-ratio quantification obtained by independent spectral decomposition of (a) single-pulse and (b) double-pulse LIBS spectra. Gray and blue bars represent the average absolute bias and standard deviation of the estimated ^{235}U abundance, respectively. The standard deviation was calculated from five replicate measurements at each uranium concentration. Both metrics are expressed in percentage points of ^{235}U abundance.

deviation. As the total concentration approached the detection limit, the reduced signal-to-noise ratio destabilized the spectral decomposition and increased the uncertainty associated with partitioning the two overlapping isotope components. Thus, the selectivity advantage of SP-LIBS became insufficient to maintain accurate and precise quantification under signal-limited conditions.

The DP results exhibited a distinctly different tendency, as shown in Fig. 4b. At high uranium concentrations, DP-LIBS produced a relatively larger bias than SP-LIBS because its broader spectral profile reduced the separability of the isotope components. Nevertheless, both bias and deviation were considerably less sensitive to decreasing total uranium concentration. As the uranium concentration decreased from 10% to 0.3%, the bias increased only slightly, from 3.3 to 4.0 percentage points, with no substantial change in the standard deviation. This result demonstrated that the enhanced emission intensity provided by DP excitation maintained fitting stability as the uranium concentration decreased, although the achievable accuracy remained limited by spectral broadening.

Collectively, the performance of isotope quantification heavily depends on the combined effects of signal strength and spectral separability rather than on either characteristic alone. SP-LIBS provides greater

isotopic selectivity and superior performance when sufficient signal is available, but its accuracy and precision deteriorate rapidly at low concentrations. In contrast, DP-LIBS provides greater robustness against signal attenuation, although its broader spectral profile limits isotope discrimination. Consequently, independent analysis of either spectrum alone cannot fully exploit the complementary advantages of the two excitation conditions, motivating a joint analytical strategy in which the SP and DP spectra are analyzed concurrently.

3.3. Joint spectral decomposition with an isotope-ratio consistency constraint

Motivated by the complementary characteristics of the SP and DP spectra, we extended the spectrum decomposition model to a joint fitting framework. In the conventional approach, the SP and DP spectra are decomposed independently, with each spectrum represented by separate components and yielding its own isotope-ratio estimate. In the proposed approach, all four spectral features ($^{235}\text{U}_{\text{SP}}$, $^{238}\text{U}_{\text{SP}}$, $^{235}\text{U}_{\text{DP}}$, and $^{238}\text{U}_{\text{DP}}$) are decomposed concurrently within a single optimization framework, as illustrated in Fig. 5a. Although the fitting component is still described using the Lorentzian model defined in Eq. (1), the key

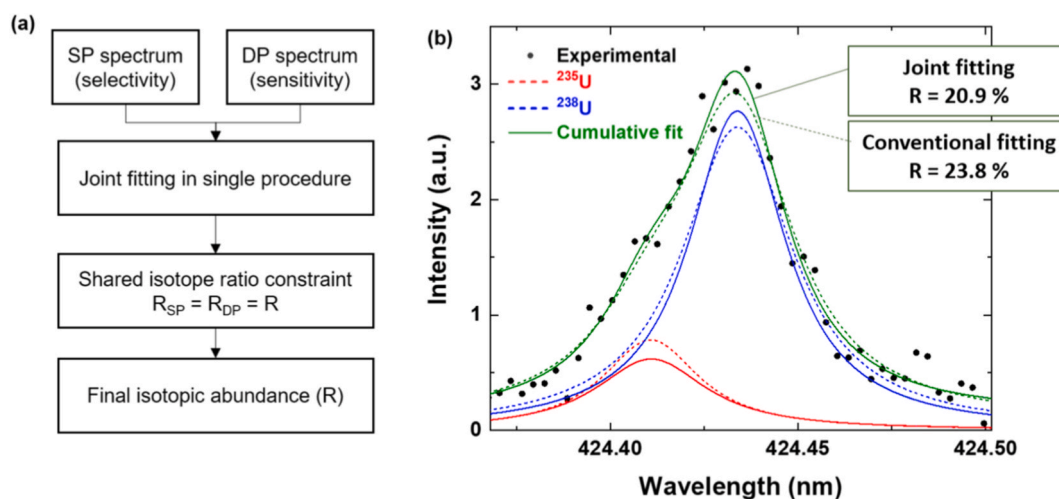


Fig. 5. Joint spectral decomposition of SP- and DP-LIBS spectra. (a) Workflow of the proposed joint fitting approach using an isotope-ratio (R) consistency constraint. (b) Representative fitting result for the U II 424.4 nm feature obtained from the 1% total U sample. Solid curves represent the proposed joint fitting, while dashed curves represent conventional independent fitting.

difference is that the joint fitting minimizes the sum of the squared residuals from the normalized SP and DP spectra:

$$J(\theta_{SP}, \theta_{DP}) = \sum_i \varepsilon_{SP}^2(\lambda_i) + \sum_i \varepsilon_{DP}^2(\lambda_i) \quad \text{Eq. (3)}$$

This formulation allows both spectral models to be optimized together. The key feature of the framework is that the isotope ratio, R , is constrained to a common value across the SP and DP models:

$$R_{SP} = R_{DP} = R \quad \text{Eq. (4)}$$

From an optimization perspective, the constraint converts two independent fitting problems into a coupled least-squares problem, in which R is shared between the two spectral models while the remaining line-shape parameters are optimized independently for each spectrum. Consequently, every trial value of R is evaluated against the residuals of both the SP and DP spectra simultaneously. Because each spectrum is independently normalized before fitting, differences in absolute signal intensity do not directly determine their relative contributions to the objective function. Instead, the residuals are weighted according to the inverse noise variance estimated from line-free regions of the corresponding normalized spectra. The narrow SP profile constrains the separation of the overlapping ^{235}U and ^{238}U components, while the higher signal-to-noise ratio of the DP spectrum provides a more reliable residual contribution under signal-limited conditions. The combined objective function therefore stabilizes the isotope-ratio estimation by reducing the influence of both broadening-induced ambiguity and signal-limited fluctuations on the spectral decomposition. The final value of R is the shared solution that minimizes the noise-weighted fitting error across the paired SP and DP datasets, rather than a simple average of the two independently estimated isotope ratios.

As a representative example, Fig. 5b visualizes how the decomposition of the DP spectrum changes when the analysis is extended from conventional independent fitting to joint fitting. The dashed curves represent the isotope components obtained by fitting the DP spectrum alone, whereas the solid curves show the corresponding components obtained when the same DP spectrum is optimized together with the paired SP spectrum under the shared- R constraint. This transition from the dashed to the solid curves reflects a redistribution of the fitted ^{235}U and ^{238}U contributions. The estimated abundance consequently shifted from 23.8% to 20.9%, reducing the absolute bias from 3.8 to 0.9 percentage points. Thus, the shared- R constraint modifies the isotope-component allocation within the broadened DP profile and yields an estimate closer to the nominal isotopic composition.

The overall improvement achieved by the joint spectral decomposition strategy was further evaluated by comparing the ^{235}U abundances obtained from SP, DP, and joint fitting in Fig. 6. The horizontal line indicates the nominal ^{235}U abundance of 20%, and the error bars represent the standard deviation of five replicate measurements. Consistent with the results in Fig. 4, the isotope abundances obtained from independent SP and DP fitting showed substantial deviations from the nominal value. The SP estimates became increasingly unstable as the uranium concentration decreased, reflecting the deterioration in signal-to-noise ratio. The DP estimates were less affected by decreasing concentration but remained systematically inaccurate because of the broadened spectral profile.

In contrast, the joint fitting results remained close to the nominal ^{235}U abundance over the entire concentration range. The absolute bias remained within approximately 1 percentage point, and the standard deviation among replicate measurements was substantially smaller than that observed for either independent fitting approach. At 0.3 wt% total U, the lowest concentration experimentally investigated in this study, the joint fitting approach yielded a mean ^{235}U abundance of 20.88%, corresponding to an absolute bias of 0.88 percentage points and a standard deviation of 1.12 percentage points. The corresponding 95% confidence interval of the mean was 19.49–22.27%. These values characterize the accuracy, precision, and uncertainty of isotope-

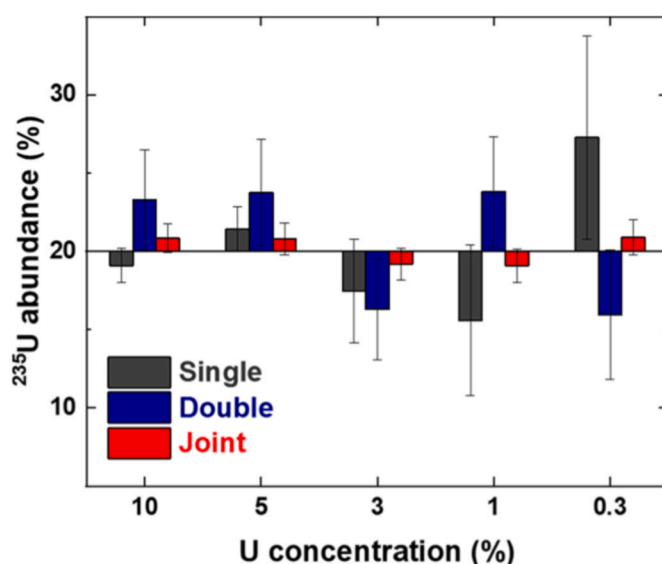


Fig. 6. Comparison of estimated ^{235}U abundances using independent single-pulse, double-pulse, and the proposed joint fitting approach over a total uranium concentration range of 0.3–10%. The horizontal line indicates the nominal ^{235}U abundance of 20%. Each bar extends from the nominal abundance to the mean estimated abundance, and the error bars represent the standard deviation obtained from five replicate measurements at each concentration.

abundance determination under the present experimental conditions. These results demonstrate that the shared- R constraint effectively combines the complementary information contained in the two spectra: the narrower SP profile provides the spectral structure required for isotope discrimination, while the stronger DP signal stabilizes the decomposition as the uranium concentration decreases. Consequently, the joint estimate is not simply an average of the independently determined SP and DP values but a physically constrained solution that best represents both spectra simultaneously. The proposed strategy therefore mitigates the sensitivity–selectivity trade-off and enables accurate and reproducible uranium isotope quantification. This analytical performance also compares favorably with that reported in previous studies of LIBS-based uranium isotope analysis [13–16].

The present validation was limited to a single nominal ^{235}U abundance of 20%, and the results should therefore be interpreted within this isotopic composition. Further investigation across a broader range of uranium isotopic compositions will be needed to assess the robustness and to determine how the performance of the joint fitting framework varies with isotopic composition. With such further validation, continued advances in laser-based spectroscopy and data analysis may help extend the capabilities of optical sensing to a broader range of analytical applications [26–29].

4. Conclusion

This study demonstrated a joint spectral decomposition strategy for mitigating the sensitivity–selectivity trade-off in LIBS-based uranium isotope analysis. SP-LIBS preserved the relatively narrow spectral structure required for isotope discrimination but became increasingly susceptible to signal limitations at low uranium concentrations. In contrast, DP-LIBS substantially enhanced uranium emission and maintained fitting stability as the concentration decreased, although the associated line broadening reduced isotopic selectivity. By fitting the paired SP and DP spectra simultaneously under a shared isotope-ratio constraint, the proposed approach combined the complementary information provided by the two excitation regimes. The framework leveraged the enhanced sensitivity of DP-LIBS to achieve a uranium detection limit of 0.008% in a soil matrix, while maintaining the estimated ^{235}U

abundance within approximately 1 percentage point of the nominal value. Overall, the present results demonstrate the feasibility of combining SP- and DP-LIBS spectra through joint spectral decomposition for uranium isotope analysis under controlled laboratory conditions. At this stage, the present study primarily serves as a proof-of-concept, and further validation will be needed before its performance can be established under field-relevant conditions. With further experimental validation across a wider range of sample matrices and isotopic compositions, together with the implementation of more compact and field-compatible instrumentation, the proposed framework may provide a basis for future rapid uranium isotope screening in nuclear safeguards, security, and related applications.

CRedit authorship contribution statement

Sung-Uk Choi: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yongheum Jo:** Writing – review & editing, Validation, Project administration, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yongheum Jo reports financial support was provided by National Research Foundation of Korea. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] H.-D. Choi, J. Kim, Basic characterization of uranium by high-resolution gamma spectroscopy, *Nucl. Eng. Technol.* 50 (2018) 929–936.
- [2] R. He, X.Y. Niu, Y. Wang, H.W. Liang, H.B. Liu, Y. Tian, et al., Advances in nuclear detection and readout techniques, *Nucl. Sci. Tech.* 34 (2023) 205.
- [3] P.B. Rose, A.S. Erickson, M. Mayer, J. Nattress, I. Jovanovic, Uncovering special nuclear materials by low-energy nuclear reaction imaging, *Sci. Rep.* 6 (2016) 24388.
- [4] A.S. Krass, P. Boskma, B. Elzen, W.A. Smit, *Uranium Enrichment and Nuclear Weapon Proliferation*, Routledge, London, 2020.
- [5] Y.J. Guan, H.J. Wang, M. De Cesare, F. Terrasi, The AMS measurement of ^{236}U at CIRCE, *Nucl. Sci. Tech.* 28 (2017) 98.
- [6] F. Claverie, A. Hubert, S. Bérail, A. Donard, F. Pointurier, C. Pécheyran, Improving precision and accuracy of isotope ratios from short transient laser ablation–multicollector–inductively coupled plasma mass spectrometry signals: application to micrometer-size uranium particles, *Anal. Chem.* 88 (2016) 4375–4382.
- [7] S. Díez-Fernández, H. Jaegler, C. Bresson, F. Chartier, O. Evrard, A. Hubert, et al., A new method for determining $^{236}\text{U}/^{238}\text{U}$ isotope ratios in environmental samples by means of ICP-MS/MS, *Talanta* 206 (2020) 120221.
- [8] D.W. Boomer, M.J. Powell, Determination of uranium in environmental samples using inductively coupled plasma mass spectrometry, *Anal. Chem.* 59 (1987) 2810–2813.
- [9] C.T. Nguyen, J. Zsigrai, Basic characterization of highly enriched uranium by gamma spectroscopy, *Nucl. Instrum. Methods Phys. Res. B* 246 (2006) 417–424.
- [10] Q. Ma, Z. Liu, T. Zhang, S. Zhao, X. Gao, T. Sun, Y. Dai, Multielement simultaneous quantitative analysis of trace elements in stainless steel via full spectrum laser-induced breakdown spectroscopy, *Talanta* 272 (2024) 125745.
- [11] K.M. Muhammed Shameem, V.S. Dhanada, S. Hari Krishnan, S.D. George, V. B. Kartha, C. Santhosh, V.K. Unnikrishnan, Echelle LIBS–Raman system: a versatile tool for mineralogical and archaeological applications, *Talanta* 208 (2020) 120482.
- [12] R.S. Harmon, F.C. De Lucia, A.W. Miziolek, K.L. McNesby, R.A. Walters, P. D. French, Laser-induced breakdown spectroscopy (LIBS)—an emerging field-portable sensor technology for real-time, in situ geochemical and environmental analysis, *Geochem. Explor. Environ. Anal.* 5 (2005) 21–28.
- [13] F.R. Doucet, G. Lithgow, R. Kosierb, P. Bouchard, M. Sababi, Determination of isotope ratios using laser-induced breakdown spectroscopy in ambient air at atmospheric pressure for nuclear forensics, *J. Anal. At. Spectrom.* 26 (2011) 536–541.
- [14] D.A. Cremers, A. Beddingfield, R. Smithwick, R.C. Chinni, C.R. Jones, B. Beardsley, L. Karch, Monitoring uranium, hydrogen, and lithium and their isotopes using a compact laser-induced breakdown spectroscopy probe and high-resolution spectrometer, *Appl. Spectrosc.* 66 (2012) 250–261.
- [15] G.C.Y. Chan, I. Choi, X. Mao, V. Zorba, O.P. Lam, D.K. Shuh, R.E. Russo, Isotopic determination of uranium in soil by laser-induced breakdown spectroscopy, *Spectrochim. Acta Part B At. Spectrosc.* 122 (2016) 31–39.
- [16] J. Song, G.C.Y. Chan, X. Mao, J.D. Woodward, R.W. Smithwick, T.G. Schaaff, A. C. Stowe, C.D. Harris, R. Zheng, V. Zorba, R.E. Russo, Multivariate nonlinear spectral fitting for uranium isotopic analysis with laser-induced breakdown spectroscopy, *Spectrochim. Acta Part B At. Spectrosc.* 150 (2018) 67–76.
- [17] F. Colao, V. Lazic, R. Fantoni, S. Pershin, A comparison of single and double pulse laser-induced breakdown spectroscopy of aluminum samples, *Spectrochim. Acta Part B At. Spectrosc.* 57 (2002) 1167–1179.
- [18] R. Ahmed, M.A. Baig, A comparative study of single and double pulse laser induced breakdown spectroscopy, *J. Appl. Phys.* 106 (2009) 033307.
- [19] J. Klus, P. Mikysek, D. Prochazka, P. Pořízka, P. Prochazková, J. Novotný, et al., Multivariate approach to the chemical mapping of uranium in sandstone-hosted uranium ores analyzed using double pulse laser-induced breakdown spectroscopy, *Spectrochim. Acta Part B At. Spectrosc.* 123 (2016) 143–149.
- [20] P.J. Skrodzki, J.R. Becker, P.K. Diwakar, S.S. Harilal, A. Hassanein, A comparative study of single-pulse and double-pulse laser-induced breakdown spectroscopy with uranium-containing samples, *Appl. Spectrosc.* 70 (2016) 467–473.
- [21] S.-U. Choi, S.-C. Han, J.-Y. Lee, J.-I. Yun, Isotope analysis of iron on structural materials of nuclear power plants using double-pulse laser ablation molecular isotopic spectrometry, *J. Anal. At. Spectrom.* 36 (2021) 1287–1296.
- [22] Z. Li, K. Wang, M. Cheng, W. Zhou, Study on the electrothermal instability in electrically exploding aluminum wires in air, *Phys. Plasmas* 33 (2026) 042103.
- [23] L. Zhao, Y. Shu, S. Xiang, C. Yao, S. Dong, Panoramic hybrid transmission topology and spatially adaptive sensitivity compensation EIT: Wide-field deep imaging via dual-array, *Appl. Phys. Lett.* 128 (2026) 143702.
- [24] A. Brown, A. Glaser, On the origins and significance of the limit demarcating low-enriched uranium from highly enriched uranium, *Sci. Global Secur.* 24 (2016) 131–137.
- [25] I. Choi, X. Mao, J.J. Gonzalez, R.E. Russo, Plasma property effects on spectral line broadening in double-pulse laser-induced breakdown spectroscopy, *Appl. Phys. A* 110 (2013) 785–792.
- [26] Z. Zhang, Z. Yang, C. Wang, W. Xu, Accelerating ultrashort pulse laser micromachining process comprehensive optimization using a machine learning cycle design strategy integrated with a physical model, *J. Intell. Manuf.* 35 (2024) 449–465.
- [27] Z. Zhang, S. Liu, Y. Zhang, C. Wang, S. Zhang, Z. Yang, W. Xu, Optimization of low-power femtosecond laser trepan drilling by machine learning and a high-throughput multi-objective genetic algorithm, *Opt. Laser Technol.* 148 (2022) 107688.
- [28] Z. Cheng, F. Chen, E. Zuo, Z. Gong, M. Xiao, C. Li, Y. Liu, P. Liu, C. Chen, X. Lv, C. Chen, The MLSE-SCAM architecture combines with the improved DRSN-TIC model for Raman spectroscopy small-sample data learning, *Expert Syst. Appl.* 279 (2025) 127462.
- [29] J. Li, X. Hu, Y. Feng, X. Chen, J. Ye, X. Wang, C. Yang, D. Zhang, Q. Cai, H. He, Z. Ye, Q. He, X. Dai, J. Pan, Highly efficient pure red light-emitting diodes enabled by multifunctional ligand-coordinated CsPbI₃ quantum dots, *Nano Energy* 140 (2025) 111055.