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Quantitative Analysis of Uranium in Uranium Polymetallic Ore by Femtosecond Laser-Induced Breakdown Spectroscopy

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Abstract

Uranium polymetallic ore is a strategic emerging industry mineral resource, and quantitative analysis of uranium (U) content is an important step in the development process of such minerals. This paper presents a quantitative analysis study on U content in uranium polymetallic ore based on femtosecond laser-induced breakdown spectroscopy (LIBS) technology combined with the Partial Least Squares Regression (PLSR) model. First, the U content in 6 groups of samples was measured using a high-purity germanium-γ spectrometer and established as reference values, then femtosecond laser was used to ablate the samples to obtain LIBS spectra; second, two normalization methods were used to preprocess the raw spectra, and the influence of spectral data before and after preprocessing on PLSR model predictive analysis was compared; subsequently, spectral data from 5 groups of samples were used as a training set to establish a quantitative model, and analysis and prediction of U content in sample #3 were performed. The results show that the relative standard deviation of 10 predictions for sample #3 and the average relative error are only 5.94% and 4.73%, respectively, demonstrating that femtosecond LIBS combined with the PLSR algorithm has excellent analytical performance for U content in uranium polymetallic ore.

Full Text

Preamble

Quantitative Analysis of Uranium in Uranium Polymetallic Ores Using Femtosecond Laser-Induced Breakdown Spectroscopy

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Abstract

[**Background**] Uranium polymetallic ores are strategic minerals for emerging industries, and quantitative analysis of uranium (U) content represents a critical step in their development and utilization. [**Purpose**] This study investigates the quantitative analysis of uranium in uranium polymetallic ores using femtosecond laser-induced breakdown spectroscopy (LIBS) combined with partial least squares regression (PLSR) modeling. [**Methods**] Initially, uranium concentrations in six samples were measured using a high-purity germanium gamma spectrometer and established as reference values. Femtosecond laser ablation was then employed to obtain LIBS spectra from these samples. Two normalization methods were applied to preprocess the raw spectra, and their impact on PLSR model performance was compared against unprocessed data. Subsequently, spectral data from five samples were used as a training set to construct a quantitative model for predicting uranium content in sample #3. [**Results**] The results demonstrate that the relative standard deviation (RSD) and mean relative error (MRE) of ten predictive values for sample #3 were only 5.94% and 4.73%, respectively. [**Conclusions**] This confirms that femtosecond LIBS combined with the PLSR algorithm exhibits excellent analytical performance for uranium content in uranium polymetallic ores, providing a valuable reference for practical applications of this technology.

Keywords: Femtosecond laser-induced breakdown spectroscopy, Uranium polymetallic ores, Uranium, Quantitative analysis, Partial least squares regression

Classification Codes: O657.38; TD868; TD983

Introduction

Against the backdrop of global climate change, nuclear energy has emerged as an essential green and clean energy source for mitigating climate issues and ensuring sustainable development of the energy industry [?]. As an indispensable fuel for nuclear power generation, uranium represents a critical factor for the stable development of the nuclear power industry. China's uranium resources account for only 4.38% of the global total, resulting in extremely high external dependency. With the rapid expansion of nuclear power programs, uranium demand has increased substantially. Uranium polymetallic minerals serve as strategic resources for emerging industries [?] and hold significant positions in the critical minerals sector. Strengthening the exploration and development of uranium polymetallic ores will play a vital role in achieving China's dual-carbon goals and advancing energy strategy [?]. However, China's uranium polymetallic ore resources are characterized by low grade, large scale, multiple mineral species, and substantial potential, necessitating accurate determination of elemental composition, particularly radioactive uranium nuclides, to provide data support for decision-making during mining and metallurgical processes.

Conventional methods for uranium content analysis in uranium polymetallic ores include high-purity germanium gamma spectrometry, inductively coupled plasma mass spectrometry (ICP-MS) [?], inductively coupled plasma optical emission spectrometry (ICP-OES) [?], atomic absorption spectrometry (AAS) [?], and X-ray fluorescence spectrometry (XRF) [?]. However, these techniques require lengthy and complex sample pretreatment processes and demand stringent environmental conditions, precluding rapid, real-time detection of target elements. In recent years, laser-induced breakdown spectroscopy (LIBS) has developed rapidly as an analytical technique that focuses high-energy lasers on sample surfaces or interiors to generate plasma, with subsequent analysis of plasma emission spectra to determine elemental species and concentrations [?]. Compared with traditional chemical analysis methods, LIBS offers advantages including minimal or no sample pretreatment, simultaneous multi-element detection, adaptability to extreme environments such as high temperature and high radiation, and real-time rapid analysis. Consequently, LIBS has been widely applied in ore analysis [?], pharmaceutical and crop detection [?], geological exploration [?], and environmental monitoring [?].

With continuous advancement in LIBS research, the technology has attracted considerable attention from researchers in uranium exploration. The Korea Atomic Energy Research Institute's Kim et al. [?] prepared five uranium ore standard samples with varying uranium concentrations using the standard addition method, excited them with a 532 nm nanosecond laser to obtain LIBS spectra, and constructed a calibration curve based on the U I 356.659 nm analytical line to determine the detection limit for uranium in such ores. Shu et al. [?] conducted quantitative analysis of uranium in uranium ores using LIBS combined with machine learning, demonstrating that partial least squares regression (PLSR) is more suitable than random forest algorithms for LIBS-based uranium quantification. To further improve LIBS sensitivity for uranium detection, Wang et al. [?] from Tsinghua University developed beam shaping and modulation techniques for laser plasma, simultaneously enhancing spectral intensity and stability of uranium signals, thereby extending the detection limit for uranium in uranium ores to 20 μg/g. Additionally, Peng et al. [?] employed nanosecond LIBS combined with random forest to simultaneously measure uranium and thorium content in typical uranium polymetallic niobium-tantalum concentrates, achieving mean relative errors of 7.26% and 5.92% compared with high-purity germanium gamma spectrometry measurements.

In recent years, breakthroughs in femtosecond laser technology have made femtosecond LIBS a research hotspot. Studies have shown that femtosecond LIBS exhibits weaker continuum background, better spectral stability, and higher sensitivity [?, ?], making it particularly suitable for analysis of high-Z nuclear materials [?]. However, research on applying femtosecond LIBS to uranium content measurement in uranium polymetallic ores remains scarce domestically and internationally. Therefore, this study investigates quantitative analysis of uranium content in six uranium polymetallic ore samples using femtosecond LIBS combined with PLSR. Five ore samples served as the training set to establish a PLSR quantitative model, with the remaining sample as the prediction set for uranium content analysis. Compared with high-purity germanium gamma spectrometry results, the relative standard deviation (RSD) and mean relative error (MRE) for the prediction set were only 5.94% and 4.73%, respectively. This research provides a novel approach for uranium analysis in uranium polymetallic ore development and utilization.

Experimental Methods

Sample Preparation

Uranium polymetallic ore samples were obtained as raw ore purchased from a Jiangxi enterprise and processed into concentrate powders, comprising six groups. Five grams of each sample powder were weighed using a 0.1 mg precision electronic balance and pressed into pellets with a diameter of 40 mm and thickness of approximately 2.5 mm using a hydraulic press (8 MPa for 3 minutes), numbered #1 through #6. Prior to pellet formation, uranium content in all samples was measured using a high-purity germanium (HPGe) gamma spectrometer (model LBE5030, Canberra Industries) and established as LIBS reference values. The HPGe gamma spectrometer features an effective energy range of 3–3000 keV, a relative detection efficiency of 45% compared to NaI(TI) crystals, and an energy resolution of 1.86 keV for the 1332.5 keV gamma ray from Co-60. Spectrum analysis was performed using Genie-2000 software version 3.3. The final sample numbers and reference uranium concentrations are presented in Table 1 .

Experimental Setup

Figure 1 [Figure 1: see original paper] schematically illustrates the femtosecond LIBS experimental apparatus, which is fundamentally similar to that used in previous research [?]. The system primarily comprises a femtosecond laser system, an echelle spectrometer, an intensified charge-coupled device (ICCD) detector, a sample stage, and a computer control system.

The laser system specifications are as follows: center wavelength 795–805 nm, pulse duration 30 fs, repetition rate 1–1000 Hz (10 Hz used in this LIBS experiment), and pulse energy 1.94 mJ. After energy adjustment using a half-wave plate (HW) and polarizer (POL) combination, laser pulses were focused vertically onto the sample surface using a 35 mm focal length lens (L1) to generate laser-induced plasma. Plasma emission was collected by a dual quartz lens system (L2 and L3, 40 mm focal length) and focused onto an optical fiber (OF, 50 μm diameter) for transmission to an echelle spectrometer (Andor Mechelle

5000) equipped with an externally triggerable ICCD detector (model DH334T-18U-03). The spectrometer covers a wavelength range of 250–950 nm with a resolution of $\lambda/\Delta\lambda = 4000$. A digital pulse delay generator (DG645) synchronized the spectrometer and laser system with a delay time of 1 µs and exposure time of 5 µs. Samples were mounted on a three-dimensional translation stage enclosed in a glass chamber connected to a filtered airflow system to prevent dispersion of radioactive powder. Each LIBS measurement accumulated 50 laser pulses to generate a single spectrum, with ten replicate measurements performed on each of the six samples, yielding a total of 60 spectra for subsequent modeling and analysis.

Algorithm and Model Metrics

PLSR is a widely employed multivariate regression method that integrates principal component analysis, canonical correlation analysis, and linear regression. Its primary advantage lies in effectively handling multicollinearity among variables and situations where the number of variables exceeds the number of samples [**?**]. The modeling process involves constructing a model with p dependent variables and m independent variables by first extracting the first component t from the independent variables and the first component u from the dependent variables to maximize their correlation, then establishing regression between the dependent variables and t. If the regression equation meets precision requirements, the process terminates; otherwise, subsequent component pairs are extracted iteratively until satisfactory precision is achieved.

The analytical approach for uranium quantification in uranium polymetallic ores using PLSR follows these steps: (1) preprocess the acquired LIBS data using maximum peak normalization and spectral area normalization; (2) partition the data into training and test sets; (3) determine the optimal number of principal components for the PLSR model using five-fold cross-validation; (4) construct a calibration curve from training set data and evaluate its performance parameters; (5) predict uranium content in the test set.

Model performance was evaluated using root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), mean relative error (MRE), and relative standard deviation (RSD). The expressions for RMSEC, RMSEP, MRE, and RSD are as follows:

$$\mathrm{RMSEC} = \sqrt{\frac{1}{m}\sum_{i=1}^{m}(y_i - \hat{y}_i)^2}$$

$$\mathrm{RMSEP} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}$$

where y_i and $\hat{y}_i$ represent the reference and predicted concentrations for the i-th sample, respectively; $\bar{y}$ is the mean predicted concentration for test samples;

and m and n denote the number of LIBS spectra in the training and test sets, respectively.

Results and Discussion

LIBS Spectra of Uranium Polymetallic Ores

Figure 2(a) [Figure 2: see original paper] displays the raw LIBS spectrum of sample #2 in the 230–750 nm wavelength range. Despite using 33 fs laser pulses as the excitation source, the femtosecond LIBS spectra of these ores exhibit numerous, densely packed, and mutually interfering spectral lines due to the rich metallic elemental composition. Additionally, a certain intensity of continuum background appears in the 300–450 nm region resulting from superposition of densely interfering spectral lines. Figure 2(b) presents a comparative spectral analysis of all six samples in the 356.6–357.4 nm range. Even after area normalization, the intensity of the characteristic uranium line U I 356.90 nm does not exhibit a strong linear correlation with uranium content, primarily due to complex matrix effects. Previous studies have demonstrated that traditional univariate methods face significant challenges for quantitative analysis when elemental spectral lines suffer severe interference and poor linearity with concentration [**?**]. Therefore, this study employs full-spectrum multivariate analysis using the PLSR method for quantitative uranium analysis in uranium polymetallic ores.

Spectral Preprocessing for Uranium Polymetallic Ore LIBS Data

Spectral preprocessing is crucial for ensuring analytical accuracy and reliability, optimizing data quality through mathematical and statistical methods to support spectral interpretation and application. Although no universal standard exists for preprocessing method selection, comparative evaluation of subsequent model performance metrics can guide the choice [**?**]. Following this principle, this study applied two normalization methods—maximum peak normalization (Max) and full-spectrum area normalization (Whole)—and compared their impact on PLSR model performance against raw spectra (Raw). Figure 3 [Figure 3: see original paper] presents the PLSR performance metrics for the three spectral types. The results indicate that maximum peak normalization yielded the lowest RMSEC, RMSEP, RSD, and MRE values at 42.07 µg/g, 128.20 µg/g, 5.94%, and 4.73%, respectively. Consequently, maximum peak normalization was selected as the optimal preprocessing method, with processed spectra serving as input variables for PLSR modeling.

PLSR Model Optimization

For PLSR models, the number of principal components is the primary factor affecting quantitative results. Excessive components lead to overfitting, while insufficient components result in poor predictive accuracy. Selecting an appropriate number of principal components enhances model performance. This study employed five-fold cross-validation on the entire training dataset to optimize the number of principal components, using root mean square error (RMSE) as the evaluation metric. The component number corresponding to minimum RMSE was selected as the model parameter. Figure 4 [Figure 4: see original paper] illustrates the hyperparameter optimization results for the PLSR quantitative model. Analysis reveals that when the number of principal components is six, the RMSE reaches its minimum value of 115.21 µg/g, establishing six as the optimal number of principal components for the PLSR model.

Partial Least Squares Regression Analysis

Sample #3 served as the prediction sample, with the remaining samples as calibration standards. The 50 LIBS spectra from calibration samples were designated as the training set, while the 10 spectra from sample #3 constituted the test set for PLSR model development and prediction.

Figure 5 [Figure 5: see original paper] presents the calibration curve for the training set under optimized hyperparameters. With the exception of sample #1 (uranium content 1344 µg/g), the multiple LIBS predictions for the remaining four samples show minimal dispersion. The training set RMSEC is only 42.07 µg/g, and the correlation coefficient between LIBS predictions and HPGe gamma reference values reaches 0.9949, demonstrating excellent reliability and calibration performance of the PLSR model.

Figure 6 [Figure 6: see original paper] displays the prediction results for the test set. While predictions for spectra #3, #5, and #8 show relatively large deviations from reference values, the remaining seven measurements are distributed closely around the reference value. The RSD and MRE for the ten LIBS predictions are 5.94% and 4.73%, respectively, with both values being relatively small. These results confirm that femtosecond LIBS combined with PLSR algorithm achieves high precision and stability for uranium elemental analysis in uranium polymetallic ores.

Conclusion

This study establishes an analytical method for uranium content in uranium polymetallic ores based on femtosecond LIBS combined with PLSR. Maximum peak normalization and spectral area normalization were employed for spectral preprocessing, with comparative evaluation identifying the optimal method. This step effectively reduces interference effects and enhances model stability. Subsequently, five-fold cross-validation was used to determine the optimal number of principal components for PLSR model optimization. Model analysis demonstrates that compared with HPGe gamma spectrometry measurements, LIBS predictions for the training set show small deviations from reference values, with a linear correlation coefficient of 0.9949 and RMSEC of 42.07 µg/g, indicating excellent calibration performance. For sample #3, the PLSR model predictions achieved RSD and MRE of merely 5.94% and 4.73%, respectively, with RMSEP of 128.20 µg/g across ten measurements. These results verify that femtosecond LIBS combined with PLSR provides high predictive accuracy and stability, offering important reference and guidance for practical applications of femtosecond LIBS technology in rapid detection and analysis of uranium in uranium polymetallic ores.

Author Contributions

Ren Shichao was responsible for overall project design and theoretical framework construction. Zhang Min and Wu Shujia prepared experimental materials and designed/optimized the experimental apparatus. Wu Shujia performed the primary experimental operations. Sun Shaohua and Peng Lingling provided technical support and conducted data analysis.

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