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Chemometric Approach for the Determination of Vanadium by the LIBS Method

Laser-Induced Breakdown Spectroscopy (LIBS) has proven to be a versatile analytical technique for the detection of trace elements in various sample matrices, including hydrocarbon materials. This study focuses on optimizing LIBS parameters to enhance the accuracy and sensitivity of vanadium (V) detection in coal and hydrocarbon-based samples. A probabilistic-deterministic design of experiments (PDDoE) was employed to fine-tune key factors such as lamp energy, delay, and the number of laser impulses. Optimal settings (lamp energy: 20 J, Q-SW1: 111 µs, ΔQ-SW: 3 µs, delay: 1 µs, and 100 impulses) significantly improved the intensity of vanadium spectral lines, particularly in samples with low concentrations, achieving a limit of detection (LoD) of 0.03 % for vanadium. Calibration models were developed using Partial Least Squares Regression (PLS-R) and Multiple Linear Regression (MLR) methods. These models achieved an accuracy of 95–98 % for vanadium quantification in coal ash and hydrocarbon samples. Validation of the developed method was performed using Atomic Absorption Spectroscopy (AAS), demonstrating good correlation between predicted and experimental values. Although the method requires sample preparation and shows lower accuracy than traditional AAS, it offers a practical solution for cases where sample dissolution is difficult, such as the analysis of glasses, enamels, and geological materials. Furthermore, the method demonstrated satisfactory results in field applications, where rapid on-site analysis with portable LIBS devices was required.

Keywords: Laser-induced breakdown spectroscopy, PLS-R, MLR, Vanadium identification, Vanadium quantification, Coal, Coal ash, Design of Experiment, Chemometrics

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a versatile analytical technique that has received considerable attention in recent studies. It is capable of analyzing a wide variety of sample types, including solids [1–3], gases [4], and liquids [5–7]. While LIBS offers reasonable sensitivity and selectivity, it faces limitations, particularly when dealing with complex samples. This challenge is especially evident in spectra containing elements at low concentrations, where noise and matrix interferences can reduce experimental accuracy [8]. Consequently, optimizing LIBS experiments to minimize the limit of detection (LoD) and enhance the reliability and repeatability of results has become a key focus in contemporary analytical chemistry research.

A critical aspect of ensuring the reliability and efficiency of experimental studies is the design of experiments (DoE). This systematic approach allows researchers to effectively plan, conduct, and analyze experiments, thereby optimizing the use of resource. The primary importance of DoE lies in its ability to control variables, minimize errors, and establish cause-and-effect relationships. By carefully designing experiments, researchers can reduce variability, identify significant factors, and improve the accuracy of their conclusions [9].

Building upon this framework, the probabilistic-deterministic design of experiment (PDDoE), developed by V.P. Malyshev [10-11], emerges as a novel approach for factorial analysis. PDDoE's capability to assess both individual and combined factor effects is particularly valuable for analyzing complex samples. Unlike traditional single-factor optimization, which considers the influence of one variable at a time, PDDoE enables a more comprehensive evaluation by accounting for interactions among variables. This multifaceted approach allows researchers to identify significant interactions that may not be evident with simpler methods, ultimately leading to more accurate models and interpretations of sample behavior. Such capabilities are crucial in fields such as cultural heritage [12] and material science [13–15]. The integration of probabilistic and deterministic components helps to balance randomness and predictability in analyses, thereby enhancing result precision and optimizing experimental resources.

To complement these techniques, chemometric methods apply mathematical and statistical approaches to extract meaningful information from complex chemical data. Techniques such as principal component analysis (PCA) [16], partial least squares regression (PLS-R) [17], and artificial neural networks [18, 19] aid in reducing dimensionality, recognizing patterns, and improving data interpretation. Chemometrics is widely employed across various fields, including spectroscopy, chromatography, and environmental science, to model relationships between variables, classify data, and predict outcomes [20, 21]. This field significantly improves the accuracy of both quantitative and qualitative chemical analyses, making it particularly applicable in spectral analysis and LIBS [22, 23].

In addition to its broader applications, LIBS has proven effective for the analysis of trace elements in hydrocarbon raw materials. It has been recognized as a promising technique for the analyses of hydrocarbons such as coal, oil, and tar [24, 25]. This method has been successfully applied to quantify carbon content in coal, demonstrating LIBS's applicability in evaluating coal quality and its energy properties [26]. Furthermore, the technique has been employed for compositional analysis of coal samples, facilitating the detection of heavy metals and both major and trace elements, thus providing a comprehensive understanding of hydrocarbon materials [27, 28].

Although there are numerous methods for analyzing petroleum materials, coal, and its ash, the application of LIBS for identification and quantification of vanadium has remained limited. This is primarily due to the low concentration of vanadium and the sensitivity challenges associated with the technique. Identifying vanadium in different samples is essential given its significant industrial and environmental relevance. Vanadium is widely utilized in steel production to increase the strength of alloys, in chemical catalysts, and in emerging energy storage technologies such as vanadium redox-flow batteries. Its presence in materials such as coal and crude oil can affect processing and quality. Additionally, vanadium pollution from industrial sources poses environmental risks, and its accumulation in ecosystems can be toxic to both wildlife and humans. Therefore, monitoring and analyzing vanadium content in various materials is crucial for resource management, pollution control, and advancing energy technologies.

LIBS has demonstrated its applicability for vanadium identification in general, such as in the analysis of medicinal plants [29]. The method employs a classification model with a high accuracy rate (up to 95 % using SNV preprocessing). A study conducted on vanadium and strontium in soils using LIBS reported the use of both univariate and multivariate data analysis methods, including Partial Least Squares Regression (PLS) and Least Squares Support Vector Regression (LS-SVR). Vanadium was successfully analyzed, achieving a correlation coefficient of 0.983 and an average relative prediction error below 2.88 %, demonstrating the high accuracy of LIBS in complex matrices for example soil [30]. However, few articles have focused on vanadium identification in hydrocarbon materials [31, 32]. Notably, research has demonstrated the use of a LIBS prototype analyzer for liquid petroleum sample analysis. This study showed detection limits for vanadium in oil and solvents as low as 0.01–0.04 ppm, indicating that LIBS can be more sensitive than other standard methods, such as ICP-OES. The method also exhibited good repeatability for vanadium, with a relative standard deviation of 1.5 % at a concentration of 100 ppm [33].

The aim of this study is to combine DoE and chemometric techniques to enhance instrument sensitivity and to develop a methodology for the identification and quantification of vanadium in coal, and coal ash samples. The integration of LIBS, PDDoE, and multiple linear regression calibration can help to improve sensitivity, spectral data quality, and greater accuracy of results.

Experimental

The sample selected for the quantitative analysis of vanadium was the “Kuznetsk” coal sample. Initially, the coal was completely ashed in a muffle furnace at 700 °C for two hours. The resulting ash was homog-

enized in a mechanical mortar and used to prepare sodium tetraborate-based glasses. A series of calibration glasses was made using mixtures of vanadium(V) oxide and anhydrous sodium tetraborate. In total, five mixtures were prepared with V(V) concentrations of 1 %, 0.75 %, 0.5 %, 0.25 %, and 0.1 %. A mixture for glass without any added vanadium was also prepared. Although this concentration significantly exceeds the levels of vanadium found in real samples, this range was deliberately chosen to gradually reduce the limit of detection and increase sensitivity. A preliminary determination of the acid-neutralizing capacity of the ash was carried out using acid-base titration to estimate the amount of tetraborate absorbed by the ash. Additionally, 2 % sodium nitrate was added to the mixture to ensure complete combustion of the coal particles. The melting of the glasses was carried out in a muffle furnace for one hour at a temperature of 1100 °C.

The concentration of vanadium in the glasses was determined by atomic absorption spectroscopy using the "Variant A140" instrument (Table 1). The analysis was repeated five times.

Table 1

V(V) concentration in the calibration glasses set

Sample	V(V) concentration, %
1	0.4607±0.012
2	0.3505±0.023
3	0.2406±0.018
4	0.131±0.009
5	0.0737±0.0042
6	0.0306±0.0026

The registration of the spectra of calibration samples was conducted using a two-pulse spectrometer "LAES Matrix Continuum" (SJSC Spectroscopic Systems, 2016, Russia) featuring a double Paschen-Runge optical scheme with optical path lengths of 250 mm and 125 mm, equipped with diffraction gratings of 2400 grooves/mm and 1200 grooves/mm, along with 7 CCD detectors from Toshiba, covering a wavelength range from 190 to 800 nm. Probabilistic-Deterministic Design of Experiments (PDDoE) using a matrix design was used to optimize the registration conditions. The matrix included six factors with five levels of variation (Table 2). The positions for the first factor – concentration – and the sixth factor – exposure time – were left vacant. These factors were chosen to simplify the construction of the overall dependence equation, as the concentration of vanadium in the sample remained constant throughout all 25 experiments, and the influence of exposure time on the analysis results is minimal.

Table 2

Factors and levels

Factor	Type	Level 1	Level 2	Level 3	Level 4	Level 5
C(V), %	V	1	2	3	4	5
Lamp Energy, J	N	15	16	17	18	19
QSW_1, μs	N	100	105	110	120	140
ΔQSW, μs	N	1	3	5	10	15
Delay, μs	N	1	2	3	4	5
Exposure, ms	V	1	2	3	4	5

Results and Discussion

The subject of optimization was the intensity of the vanadium V(II)310.224 line. The primary factor influencing the intensity of the line was the lamp energy value (Fig. 1). The other factors had no significant impact on the results of the experiment.

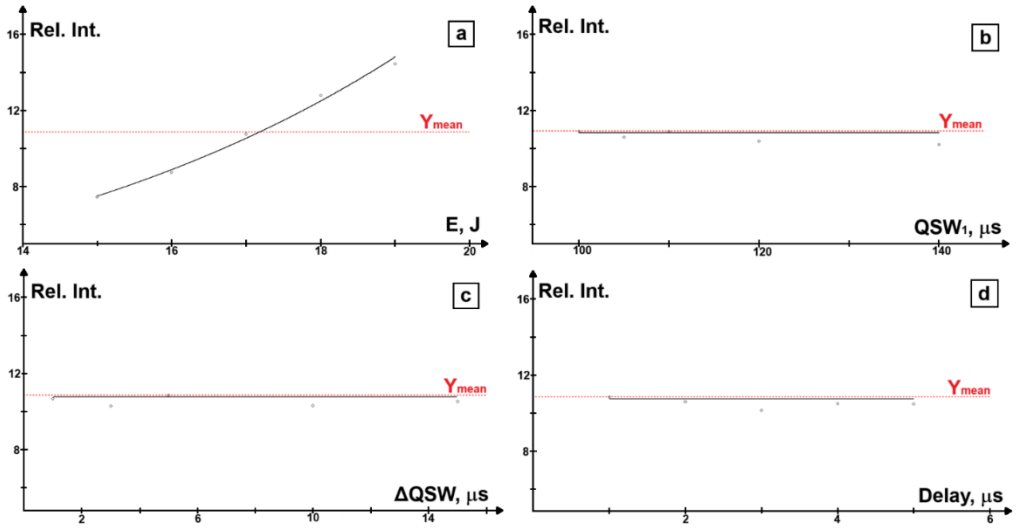

Figure 1. Partial dependencies of the $V(II)_{310.224}$ line intensity on the devise settings: Lamp Energy (*a*), QSW_1 (*b*), ΔQSW (*c*), Delay (*d*)

Overall, the optimal settings for the intensity of the $V(II)_{310.224}$ line were as follows: Lamp energy — 19J, QSW_1 — 100 μs, ΔQSW — 1 μs, Delay — 1 μs, Vacant factor — exposure time — 3 ms. Spectra of 5 calibration glasses were recorded at the calculated optimal instrument settings.

The spectral data of the calibration glasses obtained after the optimization was analyzed in the *R* environment. A model based on PLS was chosen to predict the concentration of vanadium in coal ash samples. The model was applied to determine the concentration of vanadium in the glass without addition of V_2O_5. The concentration predicted by the model (0.06 %) differed significantly from that determined by AAS (0.03 %). Furthermore, the variation in predicted results was considerable, exceeding 20 %, which can be attributed to the wider range of vanadium concentrations in the calibration glasses. This is related to the wider range of vanadium addition in the calibration glasses, as the concentration of V(V) in the initial ash was, as expected, significantly lower than the range of the calibration curve.

A second set of calibration samples was prepared with the V_2O_5 addition corresponding to the approximate concentration of vanadium in the ash. The method remained identical and the initial composition of the glasses in the new calibration set is reflected in Table 3. The final concentrations of vanadium in the second set of calibration glasses were also checked using AAS, as shown in Table 4. The appearance of the new calibration set is depicted in Figure 2.

Table 3

Composition of the second calibration set

№	Ash, g	Sodium tetraborate with V_2O_5 addition, g	Calculated concentration of the V(V) in the resulting glass, %	Lithium nitrate, %
1	1	0.64	0.05	2
2			0.04	
3			0.03	
4			0.02	
5			0.01	

Table 4

Final concentration of the vanadium in the glasses

№	V(V), %
1	0.0836±0.012
2	0.0727±0.0023
3	0.0615±0.0018
4	0.0507±0.009
5	0.0398±0.0042

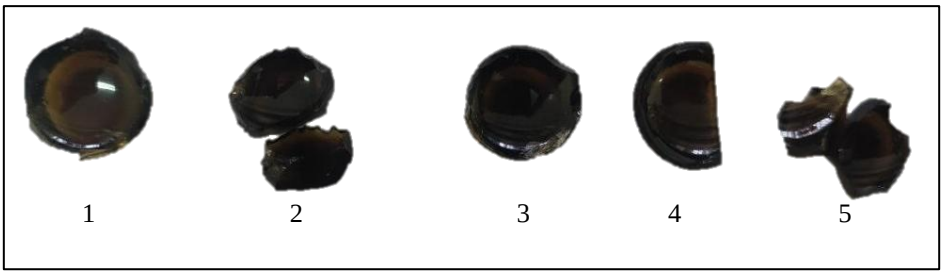

Figure 2. Second calibration set

The experimental design matrix was also modified by replacing the second vacant factor with the number of laser impulses (20–100). Additionally, the range of variation of the lamp energy value was increased to 20J. For the optimization experiment, glass with a concentration of V(V) = 0.03 % was used.

The main influence on the intensity of the $V(II)_{310.224}$ line was also due to the lamp energy, as well as the value of QSW_1 (Fig. 3).

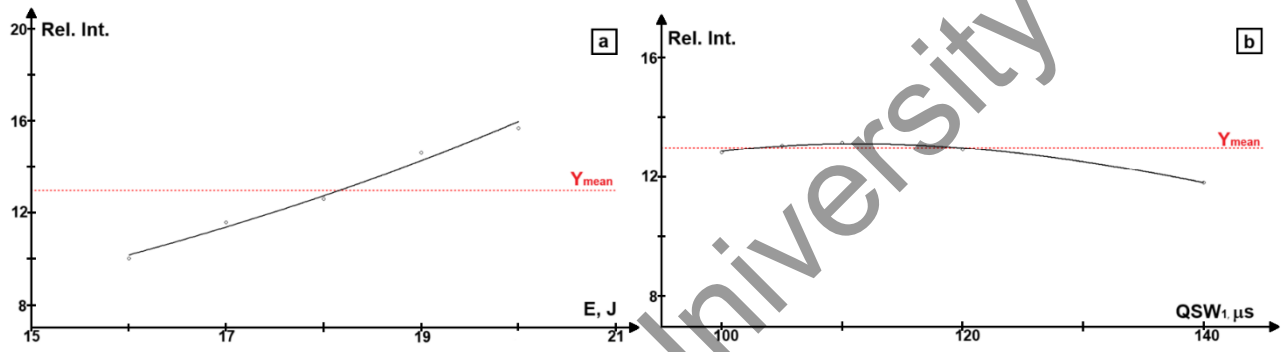

Figure 3. Partial dependence of the $V(II)_{310.224}$ line on Lamp Energy (*a*) and (*b*) value

Optimal values of factors for the analysis of the glasses with lower concentration were as follows: Lamp energy — 20 J, QSW_1 — 111 µs, ΔQSW — 3 µs, Delay — 1 µs, Number of impulses — 100. The spectra of the second set of glasses were recorded at the calculated optimal settings. The PLS-R model was retrained based on new data. The training of the model was conducted on 25 spectra (5 spectra for each calibration sample). The visualization of the resulting model characteristics is shown in Figures 4-5. The resulting model was used to determine the concentration of vanadium in the glass without V_2O_5 addition.

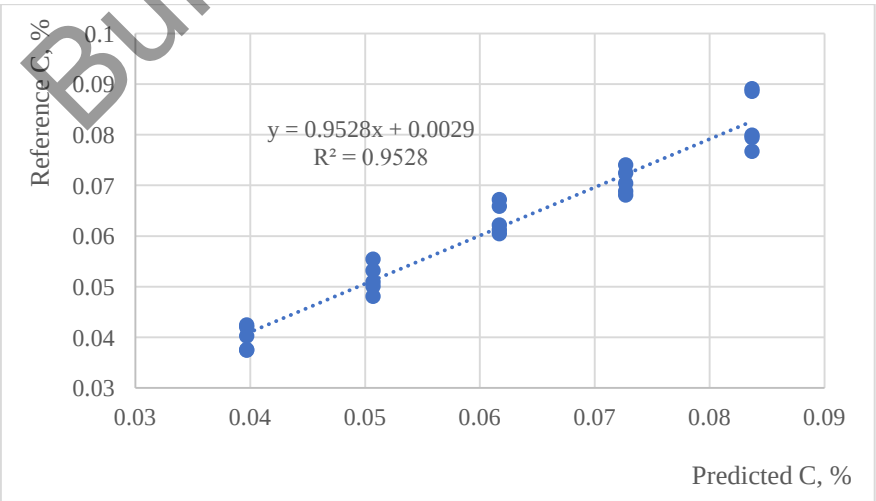

Figure 4. Predicted by PLS model and reference concentration of V(V) in calibration set

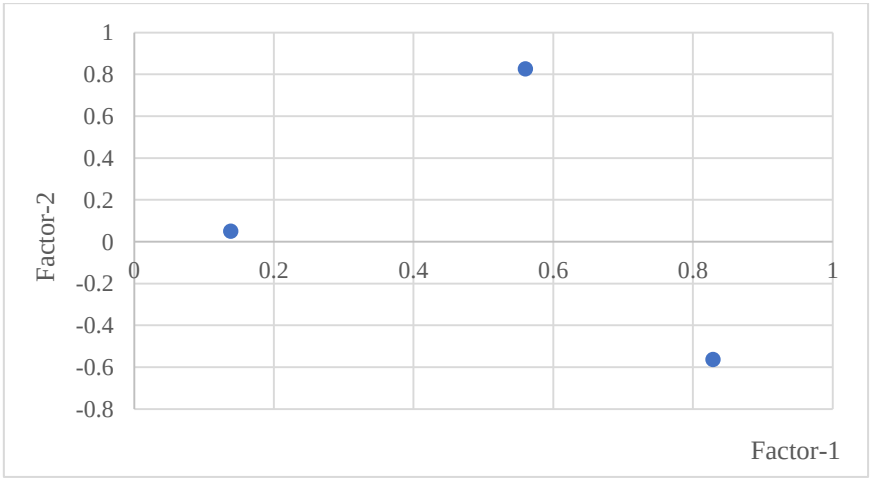

Figure 5. X and Y-loadings of the PLS model

The average V(V) concentration calculated by the model was 0.0299±0.0022 %. New set of calibration samples with lower vanadium concentration increased model accuracy and yielded a refined concentration of vanadium in the glass without the V_2O_5 addition. Additionally, Multiple Linear Regression (MLR) model was trained on the same set of data. The visualization of the model training results is shown in Figure 6. This model was also applied to predict the concentration of vanadium in the glass without any addition.

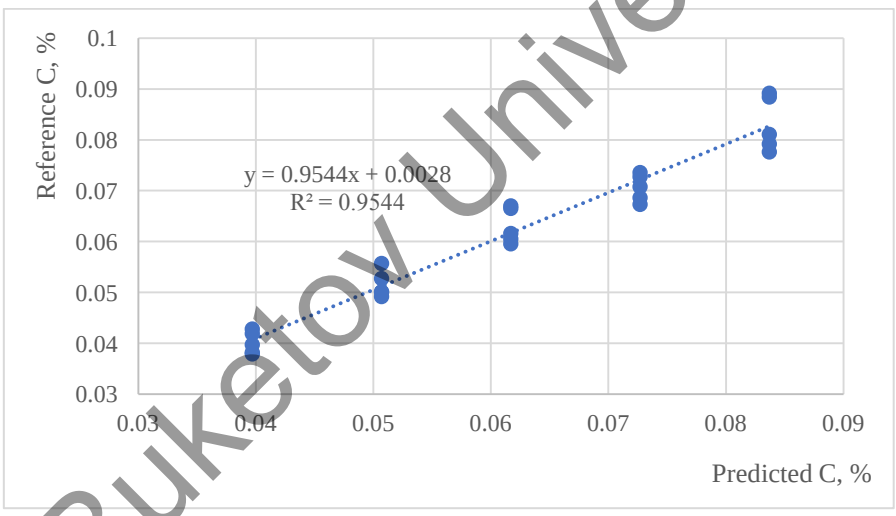

Figure 6. Predicted by MLR model and reference concentration of V(V) in calibration set

The concentration calculated by the model was 0.0297±0.0027 %. The obtained models were additionally applied to samples with unknown vanadium content. Validation of the developed methodology was carried out using atomic emission spectroscopy to analyze samples with unknown vanadium content. The final values of vanadium concentration are reflected in Table 5.

Table 5

Validation of the method

Sample	% V(V) in glass, PLS-R	% V(V) in the ash, PLS-R, %	% V(V) in glass, MLR	% V(V) in the ash, MLR, %	% V(V) in glass, AAS	% V(V) in the ash, AAS, %
Coal ash #1	0.0299 ±0.0022	0.0441 ±0.003	0.0297 ±0.0027	0.0436 ±0.004	0.0299 ±0.0016	0.0423 ±0.0023
Coal ash #2	0.0523 ±0.0094	0.0769 ±0.014	0.0532 ±0.0083	0.0758 ±0.0118	0.0521 ±0.0014	0.0774 ±0.0021
Smelter slag	0.0341 ±0.0026	0.0502 ±0.0038	0.0338 ±0.0032	0.0474 ±0.0045	0.0352 ±0.0011	0.0524 ±0.0016

An attempt was also made to determine the vanadium (V) content in rock samples collected from the Soviet-era mines without additional sample preparation or glass production (Fig. 7). Collection point is indicated in Figure 8. The results of the model calculations and their comparison with the AAS results are presented in Table 6.

Figure 7. Burned-rock samples

Figure 8. Burned-rock sampling point (49°53'28.60"N, 73°5'15.10"E)

Table 6

Vanadium content in the samples analyzed without glass preparation

Sample	% V(V), PLS-R	% V(V), MLR	% V(V), AAS
1	0.0444±0.0078	0.0451±0.0071	0.0405±0.0012
2	0.0354±0.0028	0.0351±0.0032	0.0361±0.0014

An increase in experimental errors and a decrease in the reliability of the model results can be observed. This may be explained by the fact that samples such as rocks, minerals, and ores are heterogeneous; therefore, proper preparation and experimental setup are necessary for determining vanadium in objects of unknown composition. The model could be directly applied in cases where the accuracy of quantitative vanadium determination is not critical, such as in cases of rapid determination of vanadium in samples for quick quality control of raw materials and products in situ.

Conclusions

The developed method demonstrates strong performance in quantifying vanadium in coal ash-based samples. The settings were optimized using a probabilistic-deterministic design of experiment resulting in increase of accuracy in vanadium determination in hydrocarbon-based samples. To achieve the highest intensity of vanadium spectral lines in samples with low content, the optimal instrument settings are as follows: Lamp Energy — 20 J, Q-SW$_1$ — 111 μs, ΔQ-SW — 3 μs, Delay — 1 μs, number of laser impulses — 100.

Multidimensional calibrations for vanadium quantification were built using PLS-R and MLR methods. The accuracy of the models, calculated on the basis of spectral data from samples of known composition, was 95–98 %.

An analysis of samples with unknown vanadium content was conducted using a combination of the LIBS and chemometrics, followed by validation of the methodology by atomic absorption spectroscopy. Although the accuracy of this method is lower than of classical AAS analysis, and sample preparation is also time and resource consuming, this methodology can be effectively applied to samples where dissolution for subsequent analysis presents certain difficulties. The method can be directly applied to glass and enamel samples — whether from production or archaeological finds. Additionally, satisfactory accuracy was achieved on samples without preliminary preparation, which can be applied for rapid on-site analysis with portable LIBS devices.

Supporting Information

The Supporting Information is available free at https://ejc.buketov.edu.kz/index.php/ejc/article/view/198/150

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Milana Alexandrovna Turovets** conceptualization, data curation, investigation, methodology, validation, visualization, writing-review & editing; **Vitaliy Nikolayevich Fomin** data curation, formal analysis, methodology, visualization, supervision; **Nabira Kydyrbekkyzy Kelesbek** data curation, formal analysis; **Dauletkhan Asanovich Kaykenov** data curation, formal analysis, visualization; **Daniyar Tleuzhanovich Sadyrbekov** data curation, formal analysis; **Assanali Anuarovich Aynabayev** data curation, investigation, formal analysis; **Saule Kidirbayevna Aldabergenova** project administration, writing-review & editing.

Conflicts of Interest

The authors declare no conflict of interest.

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