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Method of classification and quantitative analysis of vein quartz using LIBS and chemometric techniques

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Abstract. Vein quartz often becomes the subject of chemical analysis. Laser-induced breakdown spectroscopy (LIBS) is more rapid, cost-effective, and environmentally friendly than traditional silicate analysis. This study demonstrates the feasibility of using LIBS in combination with design of experiment and chemometric methods for the classification analysis of amorphous quartz and the quantitative determination of several constant impurities. The combination of objects and methods used in this work has not been previously published. Vein quartz samples were collected from various geographically distant locations. The sample preparation for LIBS involved cutting and polishing a flat surface of the quartz specimen. The LIBS instrument settings were optimised using design of experiment method. The concentrations of several trace elements in the training and control sets of samples were determined using atomic absorption spectroscopy (AAS). The spectra and analytical data of the training set were used for multivariate calibration using Partial Least Squares Regression (PLS-R). Sample classification was performed using Principal Component Analysis (PCA). It was shown that in the score plot in the space of the first three principal components, the samples confidently group according to their sources of origin. The results were validated on a test set of samples. The accuracy of quantitative determination of Mg, Ca, Na, K, Al, Ti using LIBS exceeded 90%. A method for the quantitative determination of several elements in quartz and an approach to identifying the place of origin of a sample are proposed.

Keywords: vein quartz, laser induced breakdown spectroscopy (LIBS), mathematical design of experiment, partial least squares regression (PLSR), principal component analysis (PCA), atomic absorption spectroscopy (AAS), silicate analysis

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Introduction

Due to its frequent use in various economic activities, vein quartz often becomes the subject of various examinations. The chemical analysis of quartz generally involves determination of its chemical composition using silicate analysis techniques [1]. This includes dissolving samples with hydrofluoric acid, removing silicon as SiF4, and subsequently quantifying trace elements. In modern analysis, atomic spectroscopy is often applied to the solutions for quantitative analysis [2]. Overall, this process is characterised by the use of a toxic reagent – HF, as well as significant duration and labor intensity. Therefore, the improvement of quartz analysis methods is of undeniable interest.

Since 1996 [3], attempts have been made to use LIBS for the analysis of various quartz types. This has shown that the method can be used to detect minor components in minerals and to characterise their qualitative composition [4]. The qualitative and quantitative determination of components by LIBS is useful for both characterization and classification of various minerals by required parameters [5]. This method is still being used in modern researches and was successfully applied to the determination of rare earth elements and other impurities in minerals [6].

There is a mention of the application of LIBS in astronomy and astrobiology for the analysis of various rocks and minerals on the surface of Mars. This has led to new insights into the complex geological history of the planet [7], as well as the information of the potential differentiation between biotic and abiotic signals used in the search for biosignatures on Mars [8].

There is also a necessity for the preliminary analysis of quartz raw materials on the manufactures of quartz products. For instance, CF-LIBS has been applied to the analysis of quartz sand used in glass production, accurately determining the components content in the raw material [9]. Additionally, this method has been used to analyse the composition of atmospheric aerosols on quartz filters [10].

Mathematical processing of spectra becomes more straightforward and simpler with the proper selection of spectrum registration modes. Optimization of the settings of various physico-chemical analysis instruments using design of experiment is currently a recommended practice, included in measurement procedures and standards. Previously [11,12], we demonstrated that probabilistic-deterministic design of experiment (PDDoE) [13] allows for the optimization of LIBS instrument settings under classical calibration conditions, where the goal of optimization is to maximise the intensity of specific analytical lines.

The analysis of quartz and quartz products remains a relevant topic, as the characterization and classification of minerals are essential in many fields of production and science. LIBS has proven to be a promising method for this task due to its rapid and straightforward multi-element analysis.

Hypothesis

By additional application of multivariate calibration methods coupled with LIBS parameters optimization by PDDoE, reliable and accurate results in the classification and characterization of quartz rocks can be achieved. The Partial Least Squares Regression (PLS-R) chemometric method aids in extracting the most informative and qualitative information from the spectral data obtained through LIBS analysis.

Methodology

Quartz vein samples were randomly collected from various deposits in the Karaganda region. Figures 1 and 2 show examples of such deposits.

Figure 1. Quartz deposits, from left to right: Tokyrau-1, East Konyrat-2, East Konyrat-3

The sample preparation for LIBS involved cutting and polishing a flat surface of the quartz specimen in the Laboratory of Technological Research at "Tsentrgeolanalit" LLC under the supervision of O.V. Kovalenko. LIBS spectra were recorded using the "LAES Matrix Continuum" instrument (Russia, "Spectroscopic Systems" LTD, 2016). The identification of analytical lines utilised the instrument software and the NIST database /14/. Instrument settings, such as lamp energy, timing of the first and second Q-switch modulators, delay, and overall exposure duration were optimised for the maximum average intensity of all analytical lines in the spectrum of one randomly selected quartz sample. A six-factor design with five levels of variation was used for the optimization by the PDDoE method. Calculations were performed using a specially developed program (Auth. Cert. RK No. 26 dated 01.10.2018). After selecting and verifying the optimal instrument settings, five samples from each deposit were used to record spectra. Some quartz specimen with LIBS impact-points are shown at the figure 2. Each sample's spectrum was recorded five times (at different points), and the resulting spectra were averaged by intensity. The averaged spectra were then used for training PLS-R model and classification using PCA. The software «The Unscrambler X» v.10.4 and the R environment [15] were used at this stage.

The dimensionality of the data was reduced using PCA, and a score plot in the space of the first three principal components was used to establish the possibility of classification.

Figure 2. Quartz specimen with LIBS impact-points

Concentrations of several trace elements in the training set were determined by AAS using a Varian AA140 instrument (USA, 2008). After the training of the PLS-R model, it was used to determine the concentrations of trace elements in the test set of samples. The obtained data was verified by AAS in triplicate, followed by an evaluation of measurement errors.

Results and Discussion

The parameters chosen for optimization were those most significantly affecting the quality of the spectrum. The range of their variation was selected based on previous experience [11,12]. The values used are presented in Table 1.

Table 1. The values of used LIBS parameters

Factor	Label	Level 1	Level 2	Level 3	Level 4
EL, J	X_1	14	16	18	20
QSW1, µs	X_2	100	120	150	180
⊗ QSW, µs	X_3	1	3	5	10
D, µs	X_4	1	2	3	5
Expos, ms	X_5	1	2	5	10

The optimised factor was the average intensity of all lines in the spectrum exceeding the background noise level. Significant dependencies were found on the energy of the lamp and the delay time of the first Q-switch modulator (Figure 3).

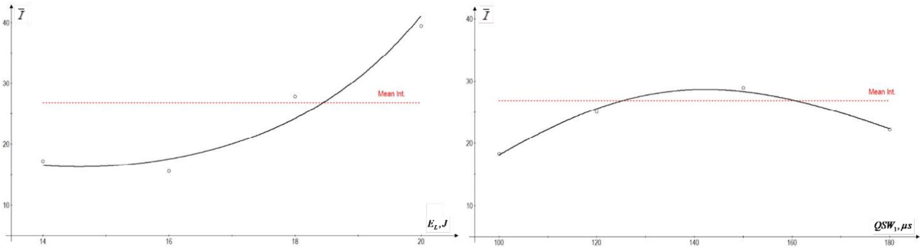

Figure 3. Partial dependencies of the average intensity on lamp energy and QSW1

The generalised equation, obtained using geometric averaging, is characterised by not impressive but sufficient for practical purposes values of R=0.591and t_R=3.27:

$$\bar{I} = \frac{20810000000000e^{1.139X_1} X_1^{-16.6} \cdot 2.181 \cdot 10^{-13} e^{-0.05775X_2} X_2^{8.214}}{23.3029}$$

The model was validated by the registration of the spectrum of a sample in five iterations, under conditions predicted by the calculation according to the generalised equation: E_L=20 J, QSW_1=140 μs. The mean intensity, with reference to Student's coefficient (5 iterations, p=0.95), was 43.4±4.43.

The spectra of all quartz samples (3-6 from each deposit) were recorded at E_L=20 J, QSW_1=140 μs in five iterations, averaged, and normalised. After this, the principal component values were calculated. The first seven principal components describe more than 99% of the variability, which is quite sufficient for any practical needs. The plot of sample positions in the space of the first three principal components is of particular interest (Figure 4):

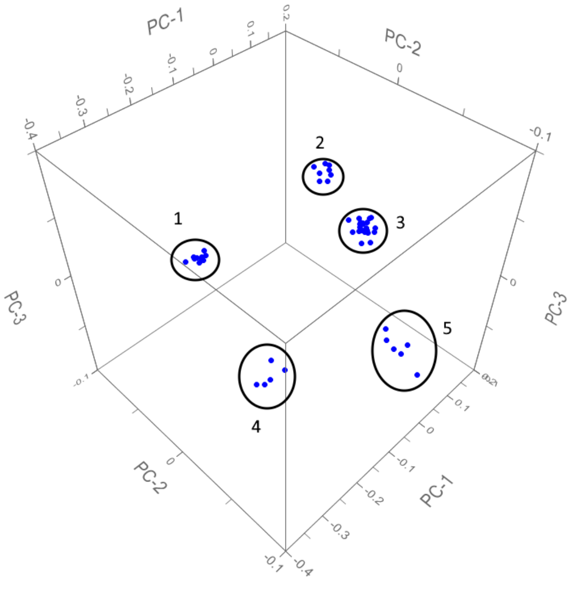

Figure 4. Grouping of the samples in the PC-1:PC-3 space

Geographically, and apparently mineralogically, similar samples were grouped together: 1 – Basaga village and Aktoky hill, 2 – Tegiszhok station and Aktas settlement, 3 – all samples from Eastern Konyrat, Tokyrau, Aktogay, 4 – samples from Ural, 5 – Zhanaarka. This tendency to cluster suggests a successful classification. For more thorough discrimination, Mahalanobis distance assessment /16/ in more than three-dimensional space and with a significantly larger number of samples is needed, but successful classification seems quite likely.

This same set of spectra was used to develop a quantitative analysis method. 4-6 quartz samples, from those for which LIBS spectra were recorded, were analysed using the classical method – dissolution in HF, distillation of SiF_4, and subsequent analysis of the obtained solutions using AAS to determine the content of Mg, Ca, Na, K, Al, Ti. One sample from each deposit was included in the test set, while the spectra and results of the silicate analysis of the remaining samples were used as a training data set for PLS-R. The quality of the model was evaluated using cross-validation. Figure 5 illustrates the quality assessment of one of the calibrations (sodium).

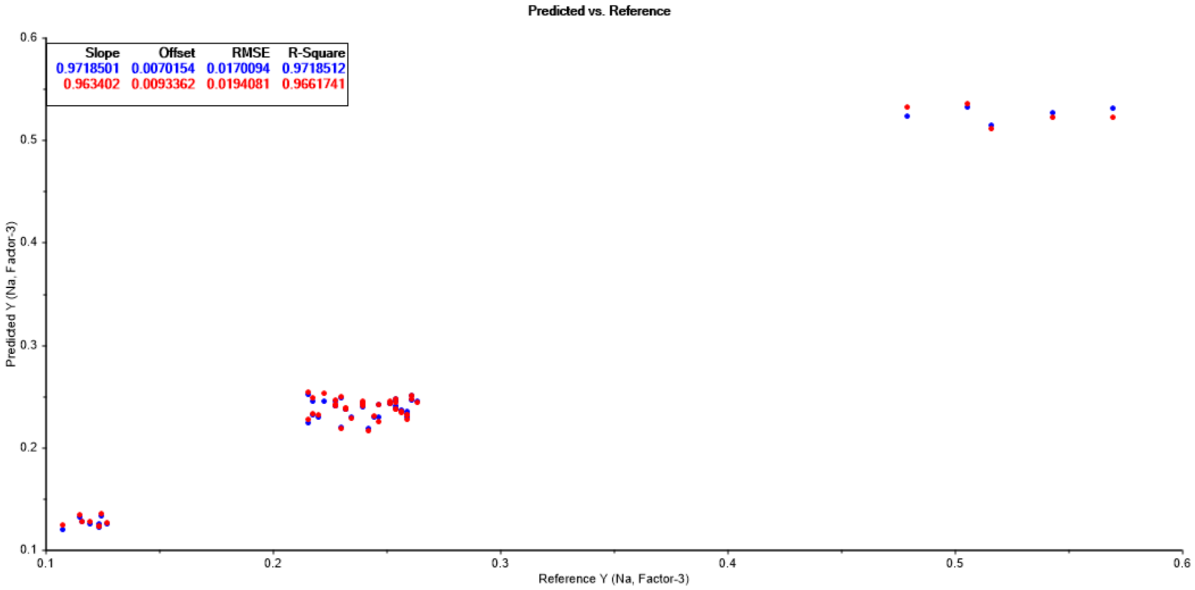

Figure 5. Results of model training for quantitative determination of sodium

Table 2 presents the results of the quantitative determination of several elements in quartz samples from the test set using AAS and LIBS methods. The confidence interval was determined traditionally regarding the Student's coefficient of 2.776 for 5 iterations (4 degrees of freedom) and a confidence probability of 0.95. In most cases, the confidence intervals overlap, and the concentrations are of the same order of magnitude in all cases.

According to Table 2, the results of the determination by the LIBS method are less accurate (as expected), but for most applications, their accuracy is sufficient. The wide confidence interval is compensated by the simplicity of sample preparation. It should be noted that the AAS results are also characterised by relatively large confidence intervals, primarily due to the inability to homogenise with a limited number of samples.

Conclusion

It can be concluded that the combination of LIBS with PLS-R is quite suitable for the quantitative determination of Mg, Ca, Na, K, Al, and Ti in vein quartz. The relative error of determination was (mg/g) 0.1821±0.0519 for Mg, 0.1662±0.0543 for Ca, 0.1646±0.0490 for Na, 0.1842±0.0534 for K, 0.1356±0.0522 for Al and 0.1752±0.0283 for Ti. The proposed quantitative analysis method is accurate and satisfactory for atomic-emission methods and can be used in the daily practice of analytical laboratories. Classification analysis for assigning the place of origin using the principal component method or related methods appears to be a promising direction for further research. A confident separation of quartz samples into groups by place of origin in the space of the first three principal components was achieved, allowing for the development of a convenient classification analysis method.

Acknowledgements and conflict of interest.

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The authors confirm that there was no conflict of interest during the study.

Authors' contributions.

Fomin V.N. – Collection of samples, general editing of the article, calculations.

Aldabergenova S.K. – Editing the article, work on the laser-induced breakdown spectrometer, calculations.

Kelesbek N.K.– Collection of samples, work on the work on the laser-induced breakdown spectrometer, sample preparation for the atomic absorption spectrometer.

Kaykenov D.A. – Work on the atomic absorption spectrometer, sample preparation for the atomic absorption spectrometer, calculations.

Turovets M.A. – selection of literature, work on the laser-induced breakdown spectrometer, calculations.

Table 2. Results of the quantitative determination of elements in quartz samples from the test set using AAS and LIBS methods

		Mg, mg/g		Ca, mg/g		Na, mg/g		K, mg/g		Al, mg/g		Ti, mg/g	
		LIBS	AAS	LIBS	AAS	LIBS	AAS	LIBS	AAS	LIBS	AAS	LIBS	AAS
1	1VosKon.test	0.0137 ±0.002	0.0141 ±0.001	0.0131 ±0.003	0.0132 ±0.001	0.2308 ±0.051	0.2851 ±0.0155	0.0639 ±0.013	0.7993 ±0.032	0.0720 ±0.008	0.0794 ±0.004	0.0137 ±0.002	0.0097 ±0.001
2	2VosKon.test	0.0149 ±0.003	0.0125 ±0.001	0.0112 ±0.002	0.0071 ±0.0008	0.2352 ±0.0009	0.1563 ±0.004	0.0665 ±0.011	0.0803 ±0.004	0.0627 ±0.011	0.0778 ±0.006	0.0125 ±0.002	0.0011 ±0.0001
3	3VosKon.test	0.0140 ±0.003	0.0172 ±0.002	0.0123 ±0.001	0.0141 ±0.001	0.2308 ±0.0032	0.2586 ±0.0143	0.0733 ±0.006	0.0691 ±0.003	0.0674 ±0.013	0.055 ±0.013	0.0138 ±0.003	0.0124 ±0.001
4	AktasTest	0.0309 ±0.014	0.043 ±0.004	0.0112 ±0.002	0.0144 ±0.0009	0.1120 ±0.0026	0.133 ±0.015	0.0665 ±0.014	0.0558 ±0.004	0.0647 ±0.008	0.0572 ±0.002	0.0139 ±0.003	0.0152 ±0.0008
5	Aktogai Test	0.0139 ±0.002	0.0168 ±0.002	0.0165 ±0.003	0.0218 ±0.002	0.1975 ±0.0012	0.0842 ±0.004	0.0699 ±0.012	0.082 ±0.009	0.0687 ±0.003	0.0672 ±0.002	0.0135 ±0.002	0.0129 ±0.001
6	AktokyTest	0.0129 ±0.003	0.0153 ±0.001	0.0113 ±0.002	0.0125 ±0.001	0.2384 ±0.002	0.2501 ±0.011	0.0618 ±0.012	0.0885 ±0.006	0.1408 ±0.008	0.1396 ±0.002	0.0125 ±0.0021	0.0153 ±0.001
7	BosagaTest	0.0120 ±0.0023	0.0177 ±0.0008	0.0131 ±0.003	0.0073 ±0.0007	0.2374 ±0.001	0.2869 ±0.011	0.0605 ±0.016	0.07 ±0.007	0.1312 ±0.026	0.0962 ±0.0012	0.0133 ±0.0021	0.016 ±0.001
8	TegisjolTest	0.0308 ±0.007	0.0378 ±0.0012	0.0118 ±0.001	0.0125 ±0.001	0.1209 ±0.0028	0.0105 ±0.017	0.0672 ±0.006	0.0633 ±0.003	0.0641 ±0.011	0.074 ±0.007	0.0117 ±0.002	0.0141 ±0.001
9	TokTest	0.0147 ±0.003	0.0115 ±0.0009	0.0124 ±0.001	0.0112 ±0.001	0.2330 ±0.002	0.1773 ±0.0105	0.0706 ±0.014	0.084 ±0.008	0.0720 ±0.01	0.08 ±0.008	0.0143 ±0.0023	0.0208 ±0.002
10	UralTest	0.0312 ±0.007	0.0483 ±0.005	0.0159 ±0.003	0.0147 ±0.0008	0.4427 ±0.0025	0.608 ±0.0134	0.1343 ±0.032	0.1592 ±0.005	0.1284 ±0.024	0.1255 ±0.002	0.0265 ±0.006	0.032 ±0.003
11	ZhanarkaTest	0.0137 ±0.002	0.0141 ±0.001	0.0131 ±0.003	0.0132 ±0.001	0.2308 ±0.051	0.2851 ±0.0155	0.0639 ±0.013	0.7993 ±0.032	0.0720 ±0.008	0.0794 ±0.004	0.0137 ±0.002	0.0097 ±0.001
	PLSR R-squre	0.93849		0.78849		0.96617		0.84396		0.93822		0.88657	

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LIBS және хемометриканы қолданып кварцты жіктеу және сандық талдау әдісі

Аңдатпа. Желілік кварц химиялық талдау объектісі ретінде жиі қолданылады. Лазерлік атомды-эмиссиялық спектроскопия дәстүрлі силикаттық талдаудан жылдамырақ, арзанырақ және экологиялық таза. Жұмыста аморфты кварцты жіктеу талдауы және бірқатар тұрақты қоспаларды сандық анықтау үшін тәжірибені жоспарлау және химометриялық әдістерімен бірге LIBS қолдану мүмкіндігі көрсетілген. Жұмыста қолданылатын әдістер объектілерінің тіркесімі бұрын жарияланбаған. Негізгі кварц үлгілері әртүрлі, географиялық жағынан бір-бірінен алыс жерлерден алынды. LIBS үшін кварцты сынама дайындау тегіс бетті кесу және тегістеу арқылы жүргізілді. LIBS құрылғысының параметрлері экспериментті математикалық жоспарлауды қолдана отырып оңтайландырылды. Үлгілердің оқыту және бақылау жиынтығындағы бірқатар қоспа элементтерінің концентрациясы AAS қолдану арқылы анықталды. PLSR әдісімен көпөлшемді калибрлеу үшін оқу жиынтығының спектрлері мен талдау деректері пайдаланылды. Үлгілерді жіктеу PCA көмегімен жүзеге асырылды. Алғашқы үш негізгі компоненттің кеңістігіндегі есеп кестесі бойынша үлгілер шығу көздеріне байланысты сенімді түрде топтастырылатындығы көрсетілген. Нәтижелер үлгілердің сынақ жинағында тексерілді. LIBS көмегімен Mg, Ca, Na, K, Al, Ti сандық дәлдігі 90%-дан асты. Кварцтағы бірқатар элементтерді сандық анықтау әдісі және үлгінің шыққан жерін анықтау тәсілі ұсынылған.

Түйін сөздер: желілік кварц, лазерлік атомды – эмиссиялық спектроскопия (LIBS), экспериментті математикалық жоспарлау, жасырын құрылымдарға регрессия (PLSR), негізгі компоненттер әдісі (PCA), атомды-абсорбциялық спектроскопия (AAS), силикатты талдау.

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Метод классификационного и количественного анализа жильного кварца с применением LIBS и хемометрики

Аннотация. Жильный кварц часто становится объектом химического анализа. Лазерная атомно-эмиссионная спектроскопия быстрее, дешевле и экологичнее традиционного силикатного анализа. В работе показана возможность использования LIBS в сочетании с планированием эксперимента и хемометрическими методами для классификационного анализа аморфного кварца и количественного определения ряда постоянных примесей. Используемое в работе сочетание объектов методов ранее не публиковалось. Образцы жильного кварца были отобраны из разных, географически удаленных друг от друга, мест. Пробоподготовка кварца для LIBS проводилась распилом и шлифовкой плоской поверхности. Настройки прибора LIBS оптимизировали с применением математического планирования эксперимента. Концентрации ряда элементов-примесей в обучающем и контрольном наборах образцов определяли с применением AAS. Спектры и данные анализа обучающего набора использовали для многомерной калибровки методом PLSR. Классификацию образцов проводили с помощью PCA. Показано, что по графику счетов в пространстве первых трёх главных компонент образцы уверенно группируются по источникам происхождения. Результаты проверяли на тестовом наборе образцов. Точность количественного определения Mg, Ca, Na, K, Al, Ti с применением LIBS превысила 90%. Предложен метод количественного определения ряда элементов в кварце и подход к определению места происхождения образца.

Ключевые слова: жильный кварц, лазерная атомно-эмиссионная спектроскопия (LIBS), математическое планирование эксперимента, регрессия на латентные структуры (PLSR), метод главных компонент (PCA), атомно-абсорбционная спектроскопия (AAS), силикатный анализ.

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