

V.N. Fomin, S.K. Aldabergenova, K.T. Rustembekov,  
A.V. Dik, Yu.Yu. Kim, I.Ye. Rozhkovoy

*Ye.A. Buketov Karaganda State University, Kazakhstan  
(E-mail: vitfomin@mail.ru)*

## Method for increasing the accuracy of quantitative determination of iron by LIBS

The problems of improving the chemometric characteristics of spectral methods of analysis are being intensively studied throughout the world. These problems are especially significant in the field of laser atomic emission spectrometry. In the article, it is proposed to use sample homogenization by fusion with sodium tetraborate. The example of iron in a mixture of oxides consisting of  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$  and  $\text{ZnO}$  has shown that fusion provides advantages over pressing, consisting in increasing the intensity of the spectral lines and increasing the accuracy of the concentration / intensity correlation, as well as an increase in the total number of spectral lines, which can be calibrated satisfactorily. Using the probabilistic-deterministic planning of the experiment and using the composite factor, it is shown that fusion substantially weakens the interrelation of the intensity of the spectral line with the instrument settings, which simplifies the choice of the spectrum registration regime. The observed regularities are explained by the high homogeneity of the vitreous samples, the more complete evaporation of the sample in the laser spark and the absence of interference in the form of a neat atomized sample, an increase in the density (and hence the concentration) of the sample. In the course of the experiments it was additionally established that for melting specimens, it was necessary to use the crucibles from alumina with caution. They dissolve rather quickly in the melt of tetraborate. Nickel crucibles can be used only if nickel is not among the elements that are determined in the sample. Based on the results of the study, there was made a conclusion about the need study of the proposed methodology and its extension to other elements of the periodic system for further.

*Keywords:* iron, sodium tetraborate, regression analysis, laser inducted breakdown spectroscopy, borate glasses, borate pressing, stochastic-determined design of experiments, chemometrics,  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$ ,  $\text{ZnO}$ .

### Introduction

Atomic emission spectroscopy (AES) is one of the most powerful modern methods of qualitative, semiquantitative and quantitative analysis in many fields of research of materials and processes, in which chemical substances are present. The wavelength of the light emitted (or absorbed) depends only on the nature of the substance, whereas the intensity is proportional to the molar concentration and essentially depends on the conditions for recording the spectrum and the chemical composition of the sample. Mutual quenching or amplification of closely spaced spectral lines of different elements, which significantly depends on the conditions for recording the spectrum, significantly complicates the interpretation of spectral data. A universal way to overcome the problems of nuclear power plants is not currently developed [1]. For the calibration of nuclear power plants, mainly classical methods based on the method of least squares are used. When searching for optimal parameters for recording spectra, experiment planning, neural networks, and the support vector method are often used. Considerable attention is paid to the use of Taguchi optimization methods. Classical methods are characterized by a lack of robustness. Methods based on the planning of the experiment require a large number of experiments and are difficult to formalize for automated processing. Neural networks, the method of support vectors and other iterative methods of resource-intensive computing are not always sufficiently developed. Thus, chemometrics used in nuclear power plants needs new methods of data processing [2, 3], including those based on planning experiments.

The well-known method of stochastic-determined design of experiment (SDDE) [4] was tested by us earlier to optimize the recording conditions of spectra in tablets with boric acid [5]. Somewhat later, a modification of the SDDE method was suggested, consisting in using as one of the factors in the composition of the sample, with a simultaneous variation in the concentrations of all the components being determined [6]. This paper describes the results of an experimental verification of the combination of the experimental planning technique proposed by us in previous studies using sample preparation by fusing samples with sodium tetraborate.

*Design of experiments*

To fully test the hypothesis of the possibility of using a composite factor in real spectrometric analysis, the composition of the samples was given by a fifth-order Latin square. As components, Fe<sub>2</sub>O<sub>3</sub>, PbO, CuO, CdO and ZnO were preliminarily calcined in a muffle furnace at 400 °C for 4 hours to remove a large part of the absorbed water. The ratios of oxides in the composition of the samples are presented in Table 1. Elements were chosen for reasons of availability and availability of several analytical lines in the studied area. The violation of the traditional SDDE sequence in some columns is conceived to simplify the software assignment of spectral lines to one of the elements and is not an error.

Table 1

**Contains of samples**

No.	CdO	ZnO	PbO	Fe <sub>2</sub> O <sub>3</sub>	CuO
1	0.5	1	1.5	2	2.5
2	2.5	1.5	1	1.5	2
3	2	2	0.5	1	1.5
4	1.5	2.5	2.5	0.5	1
5	1	0.5	2	2.5	0.5

In the experiment design, along with the composition of the sample (factor 1), the tunable parameters of the LNPP Matrix Continuum instrument were also included. The parameters used included the energy of the laser pump (factor 2), the delay time of the first gate of the Q-switch (factor 3), the delay time of the second shutter of the Q-factor (factor 4), the exposition time of the exposition start (factor 5), and the total exposition time of the CCD- matrix (factor 6). The experimental design is shown in Table 2.

Table 2

**Plan of experiments**

No. Exp	C <sub>Fe<sub>2</sub>O<sub>3</sub></sub> , %	E <sub>Lamp</sub> , J	Q-Sw <sub>1</sub> , μs	*Q-Sw <sub>2</sub> , μs	ADC, μs	Expos., ms
1	2	14	100	1	1	1
2	2	15	120	5	3	3
3	2	16	140	10	6	5
4	2	17	160	20	9	10
5	2	18	180	30	15	15
6	1.5	14	120	10	9	15
7	1.5	15	140	20	15	1
8	1.5	16	160	30	1	3
9	1.5	17	180	1	3	5
10	1.5	18	100	5	6	10
11	1	14	140	30	3	10
12	1	15	160	1	6	15
13	1	16	180	5	9	1
14	1	17	100	10	15	3
15	1	18	120	20	1	5
16	0.5	14	160	5	15	5
17	0.5	15	180	10	1	10
18	0.5	16	100	20	3	15
19	0.5	17	120	30	6	1
20	0.5	18	140	1	9	3
21	2.5	14	180	20	6	3
22	2.5	15	100	30	9	5
23	2.5	16	120	1	15	10
24	2.5	17	140	5	1	15
25	2.5	18	160	10	3	1

Note. \* — according to the instruction manual of the device, is set as Q-Sw1 + Δ, in the experiment plan and in the mathematical processing of the results the value Δ.

*Results and discussions*

Samples of mixtures with a total content of 5 % oxides were homogenized with sodium tetraborate by prolonged abrasion in a mechanical agate mortar. The resulting visually uniform powder was compressed into tablets and fused into glasses. Tableted and fused samples were analyzed on a spectrometer according to the experimental design (Table 2). The intensities of the same analytical lines of iron in the spectra of tablets and glasses were used as results for calculating the optimal mode for recording spectra using the SDDE method. Table 3 shows the experimental intensities of the three analytical iron lines obtained for tableted and glass samples.

Table 3

**The intensities of the analytical lines of iron in the samples**

No. Exp	Tablets			Glasses		
	232.7297	248.616	298.474	232.7297	248.616	298.474
1	26.7834	22.9738	35.2636	22.5508	24.1649	29.8909
2	25.6672	23.3546	36.3168	23.8812	23.2003	32.0006
3	29.4848	26.9781	42.7758	23.3945	21.9805	31.5691
4	28.1594	24.7665	39.6026	23.5652	20.4546	28.4982
5	24.9612	24.7242	37.8711	16.3399	12.6603	18.4098
6	18.8974	17.0764	27.1332	16.7599	19.7137	24.0915
7	19.5362	17.4471	26.2663	15.1686	13.8483	18.8229
8	16.6779	14.3612	24.7496	15.1585	13.8349	18.3919
9	19.6405	17.0172	26.8478	17.3719	16.4674	23.3113
10	30.1505	26.7803	43.8856	20.561	17.8244	26.7536
11	10.287	7.8714	13.979	9.0879	10.7555	15.8764
12	14.225	11.903	19.0932	11.5943	12.0602	16.6575
13	12.0274	11.1728	17.5459	11.0078	10.4301	11.9687
14	16.431	16.6086	26.8057	14.8919	15.0421	19.9856
15	18.1323	16.042	28.3804	15.1284	14.0509	21.8309
16	6.1737	6.4518	9.3534	5.9302	7.99	10.1474
17	6.2951	5.4398	10.0693	6.6341	7.8844	11.0866
18	8.8737	7.5549	13.4482	7.2166	6.7053	12.4972
19	8.6043	7.0251	11.3069	7.9879	8.239	16.8716
20	11.2234	10.0384	16.8286	9.9273	9.6332	15.8732
21	21.416	17.6696	28.1494	21.1121	22.8646	29.761
22	24.2395	24.1665	41.7188	24.5111	25.2611	38.0139
23	32.954	28.7743	49.9492	25.5413	24.4484	33.2969
24	34.7044	32.4408	53.8776	33.0388	32.2286	43.4539
25	37.7254	33.4022	56.6814	22.0021	19.5015	31.7992

Figure 1 shows the intensities of the Fe line (298.474) for tableted (*a*) and fused samples (*b*). In general, because of the congestion, the figure is less informative than the digital data in the table, therefore, for the remaining iron lines, no figures are given.

Both figures and numerical data show that the average intensity of iron lines for fused samples is lower than for tableted ones. Apparently, the volume of the evaporated sample in the case of glasses is smaller, which leads to a decrease in intensity. As practice shows with the instrument, a decrease in the intensity of the lines usually contributes to an increase in the accuracy of the analysis. It should also be noted that the intensity of the boron and sodium lines (matrix elements) in the case of glass samples is much higher than in tableted analogs. The derivation of the partial dependencies and the generalized formula using SDDE is illustrated by the example of pelletized samples and the analytical iron line at 248.616 nm. Tables 4–9 show samples of particular dependences of the intensity of the Fe line (248.616) on the factors considered.

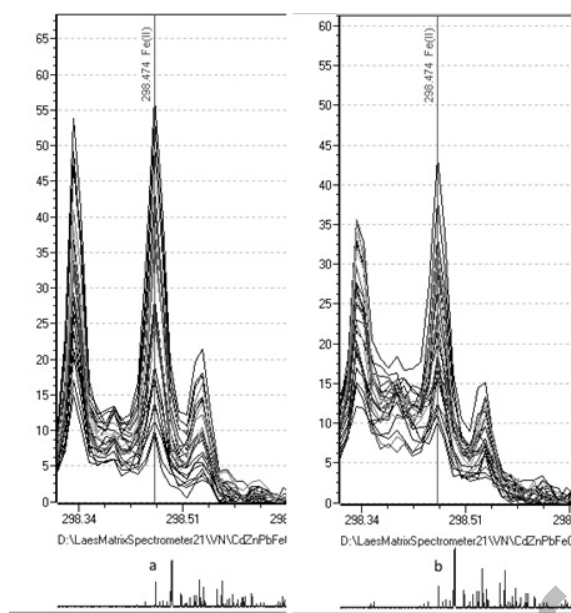


Figure 1. Intensities of lines Fe (298.474) for tablets (a) and glasses (b)

Table 4

**Factor 1. Composition of the sample**

No. of experience	The result of experience	No. of experience	The result of experience	No. of experience	The result of experience	No. of experience	The result of experience	No. of experience	The result of experience
1	22.9738	6	17.0764	11	7.8714	16	6.4518	21	17.6696
2	23.3546	7	17.4471	12	11.903	17	5.4398	22	24.1665
3	26.9781	8	14.3612	13	11.1728	18	7.5549	23	28.7743
4	24.7665	9	17.0172	14	16.6086	19	7.0251	24	32.4408
5	24.7242	10	26.7803	15	16.042	20	10.0384	25	33.4022
Med.	24.5594		18.5364		12.7196		7.302		27.2907

The formula of the partial dependence, most accurately approximating the data of Table 4,  $I = 13.59e^{-0.03484C}C^{0.8868}$ .  $R = 0.9950$ ,  $t_R = 172.771$ .

Table 5

**Factor 2. E of a lamp, J**

No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.
1	22.9738	2	23.3546	3	26.9781	4	24.7665	5	24.7242
6	17.0764	7	17.4471	8	14.3612	9	17.0172	10	26.7803
11	7.8714	12	11.903	13	11.1728	14	16.6086	15	16.042
16	6.4518	17	5.4398	18	7.5549	19	7.0251	20	10.0384
21	17.6696	22	24.1665	23	28.7743	24	32.4408	25	33.4022
Med.	14.4086		16.4622		17.7683		19.5716		22.1974

The partial dependence obtained from this table,  $I = 3.402 * 1.109^E$ .  $R = 0.9952$ ,  $t_R = 179.9879$ .

Table 6

**Factor 3. Q-SW 1, mcs**

No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.
1	22.9738	2	23.3546	3	26.9781	4	24.7665	5	24.7242
10	26.7803	6	17.0764	7	17.4471	8	14.3612	9	17.0172
14	16.6086	15	16.042	11	7.8714	12	11.903	13	11.1728
18	7.5549	19	7.0251	20	10.0384	16	6.4518	17	5.4398
22	24.1665	23	28.7743	24	32.4408	25	33.4022	21	17.6696
Med.	19.6168		18.4545		18.9552		18.1769		15.2047

According to Table 6, a partial dependence is obtained as a function of  $I = 0.02046e^{-0.01605QSW1} QSW1^{1.835}$ ,  $R = 0.8712$ ,  $t_R = 6.2610$ .

Table 7

**Factor 4. Q-SW2 — Q-SW1,  $\mu$ s**

No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.
1	22.9738	2	23.3546	3	26.9781	4	24.7665	5	24.7242
9	17.0172	10	26.7803	6	17.0764	7	17.4471	8	14.3612
12	11.903	13	11.1728	14	16.6086	15	16.042	11	7.8714
20	10.0384	16	6.4518	17	5.4398	18	7.5549	19	7.0251
23	28.7743	24	32.4408	25	33.4022	21	17.6696	22	24.1665
Med.	18.1413		20.0401		19.901		16.696		15.6297

The processing of the values grouped in Table 7 allows one to obtain a particular dependence of the intensity of the analytical line on the delay of the second shutter in the form  $I = 18.56e^{-0.01747(QSW2-QSW1)} (QSW2 - QSW1)^{0.0968}$ ,  $R = 0.9560$ ,  $t_R = 19.2396$ .

Table 8

**Factor 5. Delay of the beginning of the spectrum recording,  $\mu$ s**

No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.
1	22.9738	2	23.3546	3	26.9781	4	24.7665	5	24.7242
8	14.3612	9	17.0172	10	26.7803	6	17.0764	7	17.4471
15	16.042	11	7.8714	12	11.903	13	11.1728	14	16.6086
17	5.4398	18	7.5549	19	7.0251	20	10.0384	16	6.4518
24	32.4408	25	33.4022	21	17.6696	22	24.1665	23	28.7743
Med.	18.2515		17.8401		18.0712		17.4441		18.8012

The delay in the start of the spectrum recording, presumably influencing the intensity of the analytical line, is described by the formula  $I = 18.13e^{0.01021\tau} \tau^{-0.04641}$ ,  $R = 0.3255$ ,  $t_R = 0.6306$ .

Table 9

**Factor 6. Exposition time, ms**

No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.	No. of exp.	The result of exp.
1	22.9738	2	23.3546	3	26.9781	4	24.7665	5	24.7242
7	17.4471	8	14.3612	9	17.0172	10	26.7803	6	17.0764
13	11.1728	14	16.6086	15	16.042	11	7.8714	12	11.903
19	7.0251	20	10.0384	16	6.4518	17	5.4398	18	7.5549
25	33.4022	21	17.6696	22	24.1665	23	28.7743	24	32.4408
Med.	18.4042		16.4065		18.1311		18.7265		18.7399

Finally, the exposition time of the CCD array of the device is determined by formula

$$I = 18.15 - \frac{0.2001}{\tau}, R = 0.2328, t_R = 0.4263.$$

The final formula determining the dependence of the intensity on the factors under consideration was obtained using arithmetic averaging:

$$I = 13.59e^{-0.03484C}C^{0.8868} + 3.402 * 1.109^E + 0.02046e^{-0.01605QSW1}QSW1^{1.835} + \\ + 18.56e^{-0.01747(QSW2-QSW1)}(QSW2-QSW1)^{0.0968} - 54.2448; \\ R = 0.9816, t_R = 120.397.$$

Figure 2 allows us to graphically evaluate the obtained partial dependencies of intensity from the factors considered.

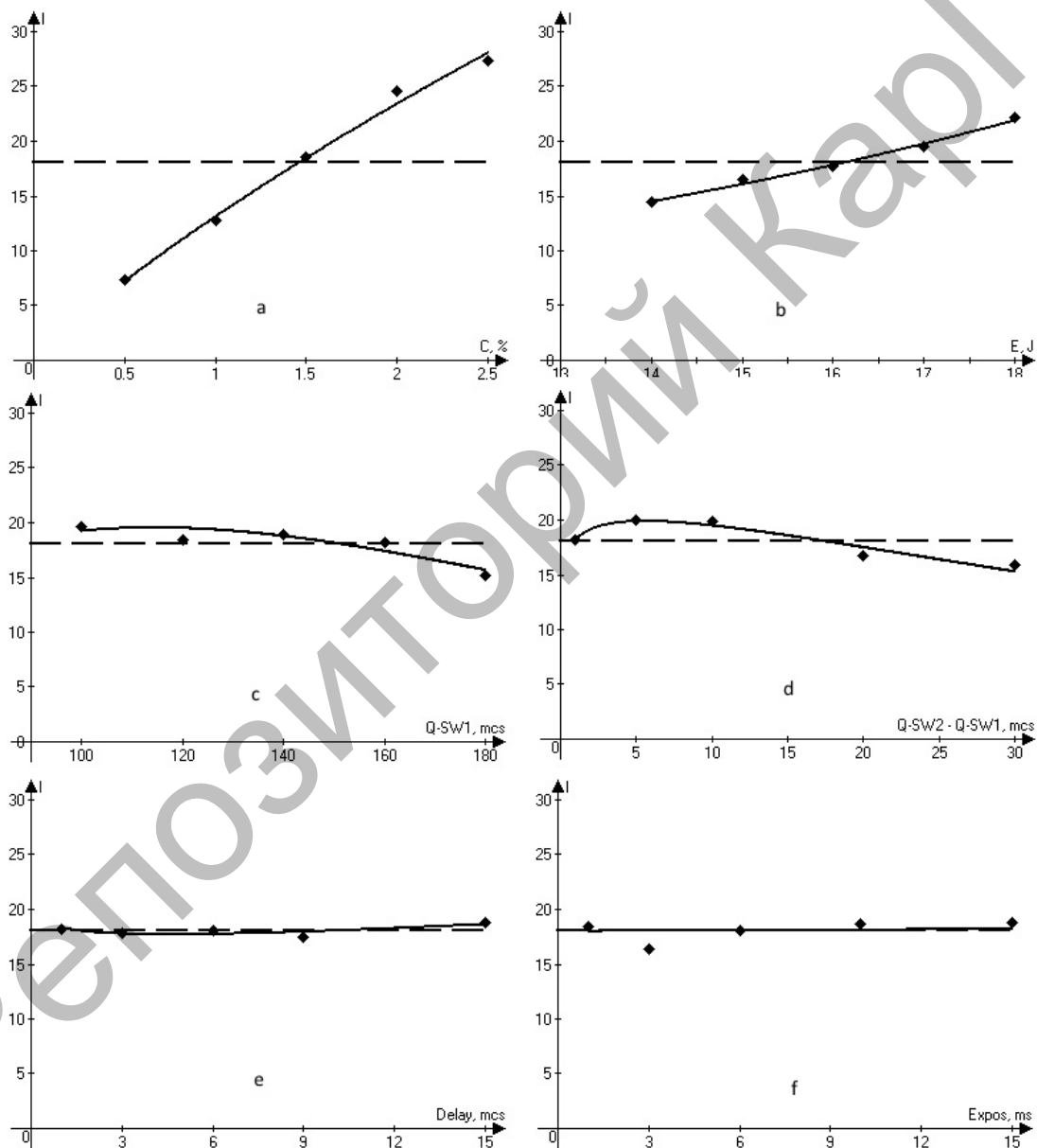


Figure 2. Partial dependence of the intensity of the analytical line Fe (248.616) on the concentration (a), the energy of the lamp (b), the delays of the first (c) and second (d) q-switches, the delay of the exposition beginning (e) and the exposition time (f)

It is easy to see from the graphs that the concentration of iron and the energy of the lamp exert the greatest influence on the intensity. The delay in the start of exposition and the total exposition time of the CCD are insignificant. A similar picture is also observed for the remaining lines of tableted samples.

In the case of vitreous samples, the picture does not change in principle. It can be stated that fusion increases the significance of a particular dependence on concentration, while at the same time negating the influence of other factors. Thus, it is difficult to optimize the spectrum registration parameters directly from the SDDE data. There are probably two options for overcoming the difficulties that have arisen: setting up an experiment with a very small increment of concentration, or mathematically processing the already available data to reduce the effect of concentration. In the framework of this article, the second option was chosen. According to the Scheibe-Lomaking equation [7], the dependence of intensity on concentration has a power-law character:  $I = aC^b$ . Its logarithm gives a function  $Ln(I) = Ln(a) + Ln(C)b$ . If  $a \Rightarrow 1$  (the simplest case) we obtain the formula  $Ln(I) / Ln(C) = b$ , where  $b$  can be determined with the help of the SDDE. In fact, the dependence that determines the intensity of the spectral lines in laser atomic emission spectroscopy has a more complicated form [2–3] than the Scheibe-Lomaking equation, so the transformation does not completely eliminate the dependence of intensity on concentration, but allows obtaining significant dependencies on other factors. Since the partial logarithm turns out to be a negative number, to increase the processing capacity, both parts were multiplied by  $-1$ . For the analytical line Fe(248.616), after the mentioned transformations of the results and substitution of them in the experimental design, we obtain formulas for the tableted samples presented in Table 10.

Table 10

The results of mathematical processing to identify significant factors

Factor	Formula	R	t <sub>R</sub>
Tablets			
Conc., %	$I = 0.5759 \times e^{-0.04422 \times C} \times C^{0.6071}$	0.9986	618.1563
Energ. lamps, J	$I = 1 / (2.449 - 0.05844 \times E)$	0.9941	146.3497
Q-SW1, mcs	$I = 0.1214 \times e^{-0.004557 \times QSW1} \times QSW1^{0.4744}$	0.9467	15.8033
Q-SW2-Q-SW1, mcs	$I = 0.6751 \times e^{-0.005193 \times (QSW2 - QSW1)} \times (QSW2 - QSW1)^{0.02393}$	0.9962	227.4676
Delay, mcs	$I = 0.6565 \times e^{0.003915 \times \tau} \times \tau^{-0.01115}$	0.9281	11.5957
Expos., ms	$I = 0.6589 + 5.424 \times \tau \times 10^{-4}$	0.3353	0.6543

The resulting Protodyakonov equation, obtained from these particular functions, makes it possible to determine parameters optimal for recording the spectrum. The maximum intensity of the Fe line (248.616) is in the range of concentrations under consideration.

It will be observed at alamp energy of 18 J, the knowledge of Q-SW1 = 100 mcs Q-SW2 = 106 mcs and an exposition delay of 1–3 μs. Similar values are obtained for glassy samples of the same composition. These parameters were decided to be used for constructing and comparing calibrations for tableted and glassy samples.

*Construction and comparison of calibrations*

Calibration was performed in five replicates to evaluate statistical characteristics. The data on the intensities of the Fe (248.616) lines in tableted and glassy samples are given in Table 11.

The coefficient of variation is calculated from the formula

$$C_v = \frac{\sigma}{\bar{x}},$$

where  $\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$ .

The relationship between concentration and intensity was established as a linear function in the MStable processor Excel. The value of the reliability of the approximation ( $R^2$ ) in all cases was above 99 %.

Table 11

**The intensities of the analytical line Fe (248.616) for the construction of calibrations**

$C, \%$	Tablets					$C_V$	Glasses					$C_V$
0.5	14.555	14.555	13.842	14.270	14.270	0.0183	10.956	10.956	10.956	10.956	10.956	0.0000
1	19.723	19.324	19.922	19.524	19.723	0.0103	15.021	15.021	15.173	15.173	15.173	0.0049
1.5	25.023	24.518	24.518	25.529	25.529	0.0181	19.009	19.202	19.202	19.202	19.009	0.0049
2	30.537	29.328	30.235	29.328	29.933	0.0162	23.063	23.063	23.063	23.296	23.296	0.0049
2.5	33.824	34.173	35.219	35.567	33.824	0.0212	27.321	27.321	27.321	27.597	27.597	0.0049
$R^2$	0.9937	0.9998	0.9985	0.9960	0.9933	0.0026	0.9999	0.9998	0.9998	0.9999	0.9996	0.0001

The coefficients of variation for glassy samples are much smaller, and the average accuracy of the approximation is somewhat higher than for tableted standards.

*Conclusion*

- The use of SDDE in the classical or modernized version does not allow obtaining a reliable calibration of the instrument for use in the entire range of settings.
- The upgraded version of the SDDE method allows choosing optimal conditions for recording spectra for calibrating the instrument.
- The proposed calibration method for tableted and glassy standards allows one to determine iron at an oxide content of 0.3–2 % in a prepared sample.
- The accuracy of calibration for tableted samples for different lines is 98–99 %, whereas for vitreous samples it exceeds 99 %.
- The covariation of intensity for the analytical line Fe (248.616) in the glasses is less than in the tablets.

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В.Н. Фомин, С.К. Алдабергенова, К.Т. Рустембеков, А.В. Дик, Ю.Ю. Ким, И.Е. Рожковой

**ЛАЭС көмегімен темірді сандық анықтаудың дәлдігін арттыру әдісі**

Спектрлік талдау әдістерін сипаттамаларын жақсарту мәселелері бүкіл әлемде қарқынды оқытылады. Әсіресе лазерлік атомдық сәулелену спектрометрия саласындағы осы мәселелер өте маңызды. Мақалада үлгінің гомогенизациясын натрий тетраборатымен балқытып біріктіру арқылы қолдану



ұсынылады.  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$ ,  $\text{ZnO}$  тұратын оксидтерінің темір коспасындағы мысалында спектрлік жолақтарының қарқындылығын жоғарлататын және концентрация/қарқындылықтың дәлділігін өсіретін, сонымен қатар қанағаттанарлықтай түзетуді жасайтын жалпы спектрлік жолақтардың санының өсуін қамтамасыз ететін балқыту үрдісі, престоуге қарағанда, артықшылықтарымен байқалды. Тәжірибені ықтималды-детерминделген жоспарлау мен факторлар құрамын қолданып, балқыту спектрлік жолақтар қарқындылығының қондырғы параметрлерінің арасындағы байланыстарды әлсіретіп, ол, өз кезегінде, спектрлерді тіркеу тәртібін таңдауды жеңілдетті. Байқалатын заңдылықтар шынытәріздес үлгілердің жоғары гомогенділігін (концентрация), лазерлік ұшқында үлгінің толық булануын, яғни атомдалмаған үлгінің шашырауы түріндегі кедергілер туындамайтындығын, сонымен қатар үлгінің тығыздығының жоғарлауын түсіндіреді. Тәжірибе барысында алундтан жасалған отбақырды сақтықпен қолдану керектігі қосымша анықталды, себебі олар тетраборат балқымасын түзе отырып, жеңіл ериді. Егер үлгі құрамында анықталатын элементтер ішіне никель енгесе, онда никельден жасалған отбақырды қолдануға болады. Зерттеу қорытындысы бойынша ұсынылған әдістемені толығымен зерттеп, периодты жүйедегі басқа да элементтерге қолдану мүмкіндігін анықтау қажет екендігін байқатады.

*Кілт сөздер:* темір, натрий тетрабораты, кемімелі талдау, лазерлік атом-эмиссиялық спектралдық талдау, боратты шыны, бораттармен престоу, тәжірибені ықтималды-детерминді жоспарлау, хемометрика,  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$ ,  $\text{ZnO}$ .

В.Н. Фомин, С.К. Алдабергенава, К.Т. Рустембеков, А.В. Дик, Ю.Ю. Ким, И.Е. Рожковой

### Метод повышения точности количественного определения железа с помощью ЛАЭС

Проблемы улучшения хемометрических характеристик спектральных методов анализа интенсивно изучаются во всем мире. Особенно значимы эти проблемы в области лазерного атомно-эмиссионной спектроскопии. В статье предложено использовать гомогенизацию пробы путем сплавления с тетраборатом натрия. На примере железа в смеси оксидов, состоящей из  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$  и  $\text{ZnO}$ , показано, что сплавление обеспечивает преимущественно перед прессованием, заключающиеся в увеличении интенсивности спектральных линий и повышении точности корреляции концентрация/интенсивность, а также увеличении общего числа спектральных линий, по которым может быть построена удовлетворительная калибровка. С применением вероятностно-детерминированного планирования эксперимента и использованием составного фактора показано, что сплавление существенно ослабляет взаимосвязь интенсивности спектральной линии с параметрами настройки прибора, что упрощает выбор режима регистрации спектра. Наблюдаемые закономерности объясняются высокой гомогенностью стекловидных образцов, более полным испарением пробы в лазерной искре и отсутствием помех в виде распыленной неатомизированной пробы, возрастанием плотности (а значит, и концентрации) образца. В ходе экспериментов дополнительно установлено, что для сплавления образцов следует с осторожностью применять тигли из алунда, так как они довольно быстро растворяются в расплаве тетрабората. Тигли из никеля можно применять, только если никель не входит в число элементов, которые определяются в пробе. По итогам выполненного исследования сделан вывод о необходимости дальнейшего изучения предложенной методики и распространения её на другие элементы периодической системы.

*Ключевые слова:* железо, тетраборат натрия, регрессионный анализ, лазерный атомно-эмиссионный спектральный анализ, боратные стёкла, прессование с боратами, вероятностно-детерминированное планирование эксперимента, хемометрика,  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CdO}$ ,  $\text{ZnO}$ .

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Репозиторий КарГУ