Optimization of experimental condition by Orthogonal Test Design in a Laser-induced Breakdown Experiment to Analyze Aluminum Alloys

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The orthogonal test design was used to optimize the parameters of the aluminum alloy LIBS. The signal to background ratio (SBR) of the line of Al I 396.15nm dependence on the experimental parameters was analyzed. It is shown that the delay time of the ICCD, the gate width of the ICCD and the laser pulse energy have a great influence on the SBR, the parameters which affect the SBR of Al I 396.15nm are, in order of the laser pulse energy, delay time of the ICCD, gate width. By optimizing the parameters of the experiment, the optimum conditions were determined and high spectral intensity and SBR were obtained under low laser energy. Besides, the sequential test was used to verify the result of the orthogonal test design, and it showed that they were in good agreement with each other. Therefore the orthogonal test design can be used as an optional scheme for the optimization of the LIBS. There are many advantages of the orthogonal test design, such as greatly reducing the workload, simple and rapid analysis, and with accurate results. It is useful to analyze the components of the aluminum alloy or other solid materials qualitatively and quantitatively under the optimum conditions.

Introduction

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Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy where the output from a pulsed laser is focused onto a sample to create an intense plasma.[1] The sample is heated by the laser pulse and a small amount of the sample evaporates, free electrons absorb energy from the laser pulse through inverse bremsstrahlung process. The energy of the electrons is transferred to the atoms and ions by collisions and more electrons are created through ionization. Newly produced electrons absorb more energy from the laser pulse and ionize more atoms. A cascade ionization happens during the pulse duration and a plasma plume is produced in front of the sample.[2,3] The advantages of LIBS over conventional spectrometric analytical methods include rapid analysis, minimal sample preparation, practically nondestructive, operational simplicity, real-time analysis, and versatile sampling of solids,[4] liquids,[5] gases,[6] or aerosols.[7] Moreover, it is able to perform in-situ elemental determinations using portable instruments and to interrogate samples remotely by stand-off analysis.[8-10]

However, many factors affect the intensity of the LIBS signal, including the delay time of the ICCD, its gate width, laser pulse energy etc. Clearly, it's important to select appropriate parameters for the LIBS experiments. The conventional method of optimizing these parameters is sequential test, but this method has the disadvantages of being time-consuming, and of ignoring mutual parameter effects. Orthogonal test design is an important method to analyze the multi-factors and multi-conditions of scientific test data.[11] Based on orthogonality, the representative samples are selected as the test points from a full-scale experiment. The advantages are that a great deal of information can be obtained from a small number of trials and that the analysis is simple and fast, but yields accurate results.

In resent years, many researchers carried out and analyzed experiments using the method of the orthogonal test design. Lee et al. analyzed the sensitivity of biometric systems based on orthogonal experiment designs.[12] Liang used orthogonal experiment design to optimize the extraction of polysaccharides from phascolosoma esulenta and evaluation of its immunity activity.[13] Wang et al. applied the orthogonal test design to the determination of trace elements in wild vegetables by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and obtained the best experimental conditions. [14] In the present experiments, the orthogonal test was used to optimize the LIBS experiments of aluminum alloys. The effects of the delay time of the ICCD, gate width of the ICCD and the laser pulse energy on the SBR of Al I 396.15nm of aluminum alloys were investigated. The optimal conditions were obtained by optimization, and then the sequential test was used to verify the results of orthogonal test design, and the results showed that they were in agreement with each other. Therefore the orthogonal test design can be applied to the LIBS experiment condition optimization of aluminum alloys in order to analyze the composition of aluminum alloys qualitatively or quantitatively.

Experimental setup

A schematic view of the experimental setup is presented in Fig.1. A Q-switched Nd:YAG laser (Big Sky Laser Technology, Ultra 100), at a fundamental wavelength of 1064 nm with a pulse duration of 8ns, repetition rate of 20Hz and maximum pulse energy of 100mJ, was used as the excitation laser. The laser was focused on the surface of the sample by a 100mm focal length plano-convex lens to produce intense, transient plasma. The light emitted from the plasma was focused by a microscope objective lens and collected by 2m long multimode silica fiber. The light is then transmitted through the fiber to the entrance of a computerized Czerny-Turner spectrograph (Andor Model SR-750-A). The spectrograph is equipped with three ruled gratings: 2400, 1200, 300 grooves/mm, which are interchangeable under computer control, providing high and low resolution spectra in the wavelength range of 200~900 nm. An intensified and gated CCD camera (Andor DH340T-18U-03) was coupled to the output end of the spectrograph. The ICCD camera has 2048×512 pixels and was cooled to -15℃ by Peltier cooler to reduce noise.

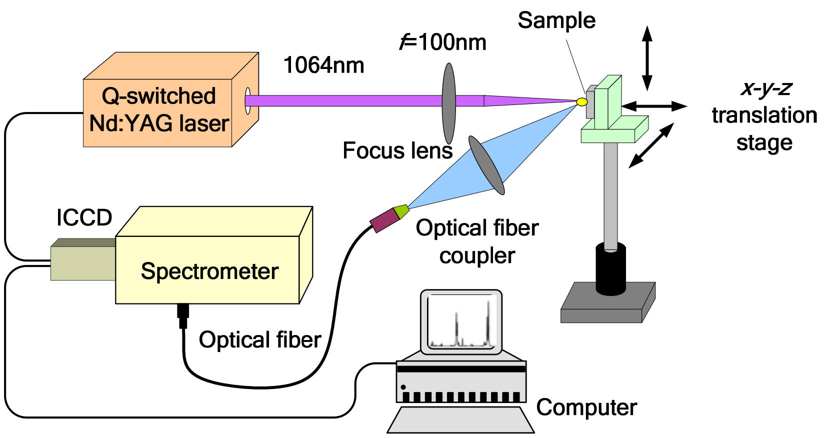


Fig.1 Schematic diagram of the LIBS experimental setup

An aluminum alloy was selected as the experimental sample and polished in order to reduce the experimental errors. The LIBS spectrum of the aluminum alloy, shown in Fig.2, shows that the spectral line of Al I 396.15nm is the strongest among the spectral lines. Besides, the lines of Mn I 372.09nm, 403.08nm, 403.31nm, 422.51nm, Cr I

373.45nm, 425.23nm, 427.29nm and Mg I 383.23nm, 383.83nm appear. The strongest emission line of Al I at 396.15nm was chosen to analyze the effects of the delay time of the ICCD, the gate width of the ICCD and the laser pulse energy on the LIBS signal of the aluminum alloy by using the method of the orthogonal test design. Twenty pulses were accumulated to obtain each spectrum, and five such spectra were measured for each experimental condition in order to increase the sensitivity and reduce the standard deviation.

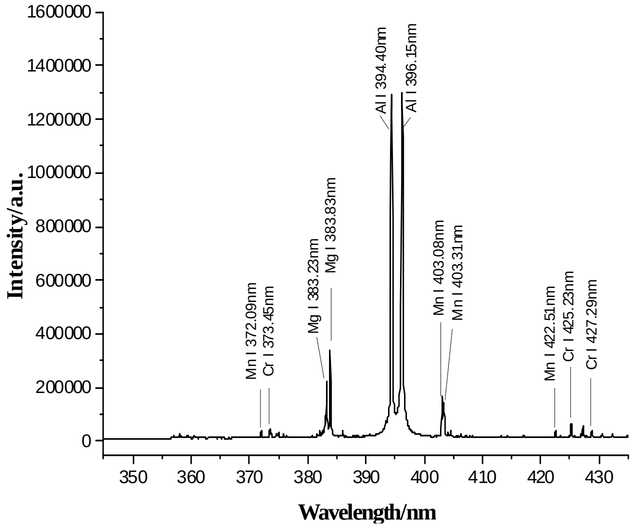


Fig.2 LIBS spectrum of aluminum alloy at 4μs delay time, 8μs gate width and 20.7mJ laser pulse energy.

Experiment and analysis

The orthogonal test design

The spectrum of the plasma consisted of both atomic spectral lines and the continuum background, the latter is primarily due to bremsstrahlung and recombination events.[15] In the process of the plasma expansion, the continuum background decays with time more quickly than spectral lines. Therefore， choosing the appropriate delay time of the ICCD and the gate width of the ICCD can effectively improve the spectral signal, weaken the interference of background continuum and overall improve the SBR. In addition, only if the energy is above the threshold of the plasma formation, will the plasma appear. When the pulse energy is low, the emission intensity increases with the increasing pulse energy. For higher laser powers, the emission signal reaches a saturation regime, attributed to the self-absorption of the emission by the plasma formed in front of the sample, or due to poor coupling of the laser caused by plasma shielding.[16] Hence it is essential to select optimal laser pulse energy to improve the SBR.

The purpose of this experiment is to investigate the effects of the delay time of the ICCD, the gate width of the ICCD and the laser pulse energy on the LIBS signal, and to optimize the experimental condition. These three factors were denoted as A, B and C respectively. Five levels were selected for each factor, donated them as 1, 2, 3, 4, and 5 respectively. The factors and levels of L_{25} (5^3) are listed in Table 1.

Table 1 Factors and levels designed of L_{25} (5^3) orthogonal test

Level	Factors		
	Delay time of the ICCD (A)/ µs	Gate width of the ICCD (B)/ µs	Laser pulse energy (C)/mJ
1	1	3	6.7
2	4	7	11.5
3	7	11	16.3
4	10	15	20.7
5	13	19	24.8

The SPSS Statistics software package was used to design and analyze the experiment. The factors and levels were entered into the SPSS Statistics software package to generate the orthogonal table. The experiment was carried out based on parameter combinations of the orthogonal table. The SBR of the Al I 396.15nm line was calculated, and then the data were inputted into the orthogonal table. The orthogonal table containing experimental index is shown in table 2.

Table 2. Orthogonal table containing experimental index

Experimental number	Delay time of the ICCD (A)/ µs	Gate width of the ICCD (B)/ µs	Laser pulse energy (C)/mJ	SBR of the Al I 396.15nm line
1	1* (1)	3 (11)	3 (16.3)	36.73
2	1	2 (7)	2 (11.5)	50.53
3	1	4 (15)	4 (20.7)	57.33
4	1	5 (19)	5 (24.8)	37.83
5	1	1 (3)	1 (6.7)	42.66
6	2 (4)	3	1	18.13
7	2	4	2	82.07
8	2	5	3	90.96
9	2	2	5	4.86
10	2	1	4	86.79
11	3 (7)	1	2	89.87
12	3	5	1	62.51
13	3	3	4	67.69
14	3	4	5	87.72
15	3	2	3	83.33
16	4 (10)	3	2	25.28
17	4	4	3	22.45
18	4	1	5	17.93
19	4	5	4	57.76
20	4	2	1	76.80
21	5 (13)	4	1	30.42
22	5	2	4	62.31
23	5	3	5	95.21
24	5	5	2	4.69
25	5	1	3	82.44

* The label of the levels

The factors and variance were analyzed by using the SPSS Statistics software package, three tables were created: 1) the variables table (Table 3); 2) the variance analysis table (Table 4); and 3) the univariate statistics table (Table 5).

Table 3 Variables table

Between-Subjects Factors

		Value Label	N
Delay time of the ICCD	1.00	1	5
	2.00	4	5
	3.00	7	5
	4.00	10	5
	5.00	13	5
Gate width of the ICCD	1.00	3	5
	2.00	7	5
	3.00	11	5
	4.00	15	5
	5.00	19	5
Laser pulse energy	1.00	6.7	5
	2.00	11.5	5
	3.00	16.3	5
	4.00	20.7	5
	5.00	24.8	5

Table 4 Variance analysis table

Tests of Between-Subjects Effects

Dependent Variable:SBR

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	11025.395*	12	918.783	1.178	.390
Intercept	75549.214	1	75549.214	96.897	.000
A	4656.620	4	1164.155	1.493	.265
B	860.353	4	215.088	.276	.888
C	5508.422	4	1377.105	1.766	.200
Error	9356.191	12	779.683		
Total	95930.800	25			
Corrected Total	20381.585	24			

* R Squared = .541（Adjusted R Squared = .082）

Table 5 Univariate statistics table

1. Delay time of the ICCD

Dependent Variable:SBR

Delay time of the ICCD	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
1	37.080	12.487	9.872	64.288
4	74.441	12.487	47.233	101.649
7	64.623	12.487	37.415	91.830
10	55.524	12.487	28.316	82.732
13	43.194	12.487	15.986	70.402

2. Gate width of the ICCD

Dependent Variable:SBR

Gate width of the ICCD	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
3	54.193	12.487	26.985	81.401
7	56.086	12.487	28.878	83.294
11	61.302	12.487	34.094	88.510
15	58.987	12.487	31.779	86.195
19	44.294	12.487	17.086	71.501

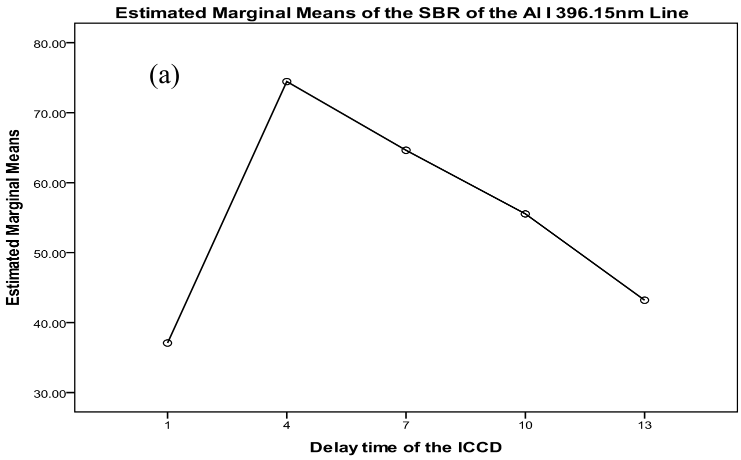
3. Laser pulse energy

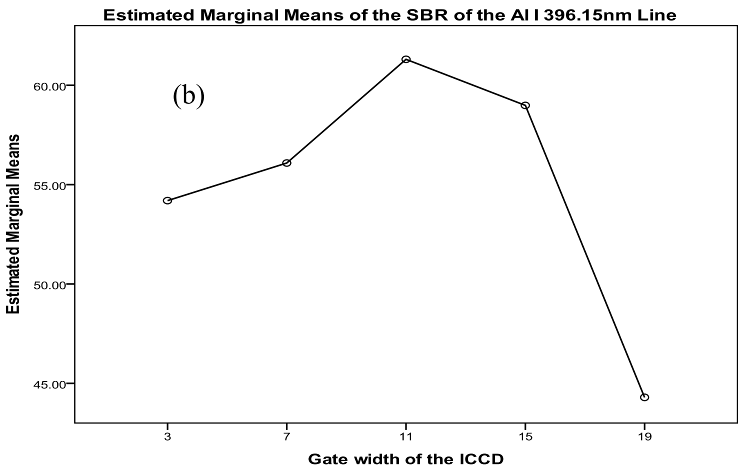
Dependent Variable:SBR

Laser pulse energy	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
6.7	28.557	12.487	1.349	55.765
11.5	48.618	12.487	21.410	75.826
16.3	67.328	12.487	40.120	94.535
20.7	66.291	12.487	39.084	93.499
24.8	64.069	12.487	36.861	91.277

The results of the variance analysis of the three factors are shown in table 4. Type Ⅲ sum of squares calculates the sum of squares of an effect adjusted for all other effects regardless of order, and the df is the degree of freedom, and F means the ratio of variance of the factors and the error variance. It is concluded from the order of type Ⅲ sum of squares of A, B and C that the order of influence is as follow: C>A>B. This means that the influencing order to the LIBS signal is the laser pulse energy > the delay time of the ICCD > the gate width of the ICCD.

The mean value of five levels for each factor, standard errors and 95% confidence interval are compiled in a univariate statistics table. According to the mean value, the optimal combination is $A_2B_3C_3$, which corresponds to a 4μs delay time of the ICCD, 11μs gate width of the ICCD, 16.3mJ per laser pulse. As shown in Fig.3, according to the estimated marginal means of the SBR of Al I 396.15nm variation with the delay time of the ICCD, the gate width of the ICCD and the laser pulse energy, we can easily get this result, too.





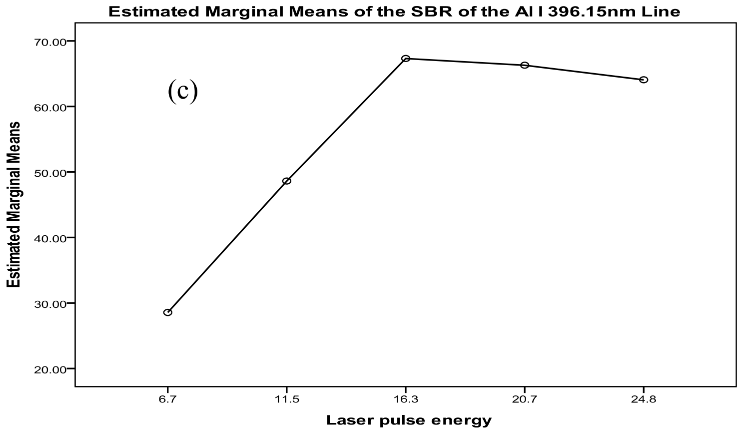


Fig.3 Estimated marginal means of the SBR of Al I 396.15nm variation with the (a) delay time of the ICCD, (b) gate width of the ICCD, and (c) laser pulse energy.

The sequential test

The sequential test was also carried out in order to verify the correctness of the orthogonal test design, the delay time of the ICCD, the gate width of the ICCD and the laser pulse energy were optimized in turn. The dependence of the SBR of Al I 396.15nm on the delay time of the ICCD is illustrated in Fig.4. In this experiment, the gate width of the ICCD was 8μs, the laser pulse energy was 20.7mJ and kept them unchanged, the delay time of the ICCD changed from 0.5μs to 24μs.

As shown in Fig.4, the SBR of Al I 396.15nm reaches the maximum value when the delay time of the ICCD is 4μs. This is because that both the atomic emission lines and the continuum background decay with increasing delay time of the ICCD, while the continuum background decays very rapidly, it decays to a small value in a short time, thus 4μs was chosen as the optimal delay time of the ICCD. Compared with the orthogonal test design method, more delay time values were selected to carry out the experiment, it’s more time-consuming and complex.

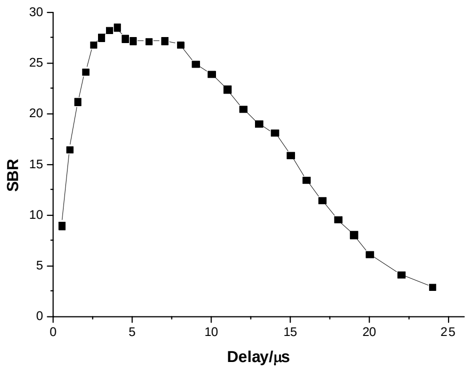


Fig.4 SBR of Al I 396.15nm variation with the delay time of the ICCD at 8μs gate width and 20.7mJ laser pulse energy.

The optimal delay time of the ICCD was selected to replace the previous one, and kept the laser pulse energy unchanged. The dependence of the SBR of Al I 396.15nm on the gate width at 8μs delay time and 20.7mJ laser pulse energy is illustrated in Fig.5.

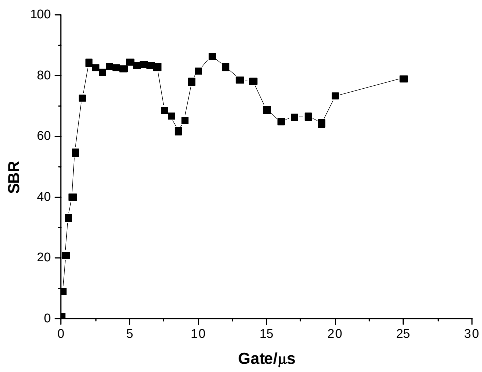


Fig.5 SBR of and Al I 396.15nm variation with the width of the ICCD at 4μs delay time and 20.7mJ laser pulse energy.

It can be seen that the SBR of Al I at 396.15nm reaches the maximum value at 11μs gate width. The continuum background is the result of the blackbody emission, the bremsstrahlung and the recombination emission. At the beginning of the plasma formation, the continuum background is mainly caused by the bremsstrahlung and the delay time increases with the increase of the gate width, while the temperature of the plasma decreases rapidly, which leads to the strongest radiation wavelength of the blackbody radiation moves toward the long-wavelength, and then causes the fluctuation of the continuum background, and finally makes for the fluctuation of the SBR of Al I 396.15nm. Therefore gate width at 11μs is the optimal condition. But it is more time-consuming since more than 30 gate width values were investigated and calculated the SBR in order to reflect the trend of the change.

The emission spectra of laser-induced plasmas were dependent on the laser pulse energy was also investigated. Aiming to enhance the SBR, it is worthwhile to discuss the effect of laser pulse energy to obtain the maximum signal and reduce the continuum background. The optimal delay time of the ICCD and the gate width of the ICCD obtained from the previous work were selected, the dependence of the SBR of Al I 396.15nm on the laser pulse energy is illustrated in Fig.6. The higher laser energy will generate optically thick plasma and cause self-absorption, the SBR of Al I at 396.15nm increases to the maximum and decreases afterwards. The best SBR is obtained with 16.3mJ laser pulse energy. So in this work we selected 16.3mJ as the optimal laser pulse energy.

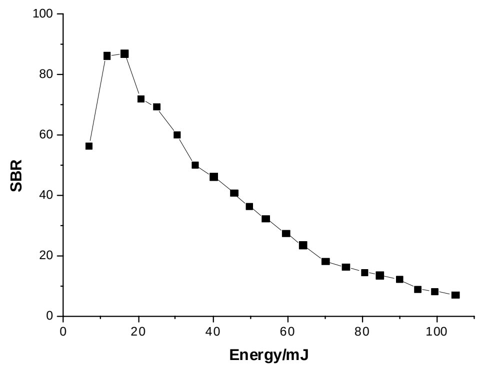


Fig.6 SBR of Al I 396.15nm variation with the energy of the laser pulse at 4μs delay and 11μs gate width.

To sum up, the optimum conditions of this experiment are 4μs delay time, gate with of 11μs and laser pulse energy of 16.3mJ. The result is in agreement with that of the orthogonal test design. It demonstrated that the orthogonal test design can be used to optimize the experimental conditions of laser-induced breakdown spectroscopy. From the analysis above, it is easily funded that the analysis process using orthogonal test design is simple and fast, and yields accurate results.

Conclusion

The orthogonal test design was used to optimize the parameters of the LIBS of the aluminum alloy. The effects of the delay time of the ICCD, gate width and the laser pulse energy on the SBR of Al I 396.15nm were investigated. The results show that all these parameters have great influence on the SBR, the parameters which affect the SBR of Al I 396.15nm are, in order of the laser pulse energy, delay time of the ICCD, gate width. The best SBR of Al I 396.15nm was obtained at 4μs delay time, 11μs gate width and 16.3mJ laser pulse energy. The optimum experimental conditions were obtained at low laser pulse energy and the repeatability was good. In addition, the sequential test was used to verify the correctness of results of the orthogonal test design and it shows that they are in good agreement with each other. There are many advantages of the orthogonal test design, such as it greatly reduces the workload, the process of the analysis is simple and rapid, and yields result accurate results. Therefore the orthogonal test design can be used as an optional scheme for the optimization of the LIBS.

Acknowledgements

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