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Use laser induced breakdown spectroscopy in detection of heavy metals contents in Sudanese cement

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Abstract

Cement is an important industrial product in construction, streets, roads, bridges, etc. It is of great importance, so it is necessary to know its heavy metal components. In this work, Laser Induced Breakdown Spectroscopy (LIBS) was used to detect, and identify, the heavy metals in Sudanese cement samples that collected from different local markets in Khartoum state. Four cement samples were used as study samples (Atbara, Barbar, Mas and Sakhr Al Sudan) cement. Nd: YAG laser in Q-switched mode was used as the laser source. The laser parameters were 8 ns pulse duration time, 10 Hz pulse repetition rate, 266 nm laser wavelength and 30 mj pulse energy. Ocean Optics LIBS 2000+ system was used as spectrometer. The detector has a gated CCD camera having 14,336 pixels. At a 90°angle to the laser pulse the emission spectra was observed. The recorded spectra samples were analyzed using NIST data.

Neutral atoms Like (Ca, Fe, Si, Na, Ti, Cr, V, Sr, Zr, Kr, K and Cs) that were detected from the analysis of samples spectra. that were found in all samples. In addition to the ions: (Ca^{+1}, Fe^{+}, Si^{+1}, Na^{+1}, Ti^{+1}, Cr^{+1}, and K^{+1}).

The heavy metals like: metals (Cr, Fe, Ti, Mn, V, Xe, Y and Zn) were appeared in the four samples.

To identify the relationship between the laser pulsed energy and the intensity of the LIBS signal, the Mas cement sample was irradiated by different pulse laser energies (10, 15, 20, 25, 30 and 32 mJ). Respectively and 200 ns delay time. We observed when the laser pulse energy increase the line intensity of the LIBS was increase.

Keywords: heavy metals, Sudanese cement, laser induced breakdown spectroscopy, laser energy, plasma temperature, electron density

Introduction

Environmental pollution with heavy metals in recent years has led to increasing global environmental and health concerns. Heavy metal is a term for any metallic chemical element that has a high relative density. [1].

Cement industry is an important binding agent in construction and is manufactured by burning inorganic raw materials at temperatures up to 1500 degrees Celsius. The carbon-based materials are one of the basic raw materials in cement production [2]. Although cement is used in various fields of construction, it may be a source of pollution with heavy metals due to the emission of dust and gases during the manufacturing process. [1]. although heavy elements are found naturally throughout the earth's crust. Human activities lead to human exposure and environmental pollution [3]. Heavy metals can affect mental and nervous functions [4]. the cement industry is part of the industries known for its problems in the introduction of heavy metals as a result of dust emission from its operations [5].

Cadmium, lead, and mercury, chromium, copper, manganese, nickel, leads and zinc, among others. These metals especially known to have deleterious effect in environmental studies these metals have been identified in the emission from cement plants [1]. Therefore, the detection of heavy metals in cement is of great importance. There are several analytical instrument techniques that can be used to identify these hazardous materials [6] such as inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF) [7, 8].

Laser-induced breakdown spectroscopy (LIBS) is atomic analytical technique a multielemental and with simultaneous detection of all the elements in real-time in any type of sample matrix including solid, liquid, gas, and aerosol [9].

libs is one of the atomic emission techniques that has found wide interest in many fields such as research, industry and others because it has many advantages over other analysis techniques [10]. LIBS technique is based on collecting atomic emissions in a plasma spark. All elements are emitted in the spectral range (200-900) nm and therefore by using a detector that covers the entire spectral range we can detect and identify the elements by their relative abundance [11]. LIBS technology is used in quantitative and qualitative analysis, and it is a rapid technique to know the components of samples and is used in all kinds of materials, solid, liquid, gas and others.in this work we used LIBS to detection the heavy metals in Sudanese cement samples.

Experimental

Samples

The Sudanese cement were selected in this study, fine powder of Atbara, Barber, Mas and Sakhar AL Sudan cement samples were collected from local market in khartoum. Sample pellets of 20mm diameter were produced by pressing 3.0g of each cement using hydraulic pressure. For pressing of pellets uniform load at pressure of 12 tons was applied for 2.0 minutes duration.

Experimental setup

The experimental setup consisted of Q- switched Nd: YAG nanosecond laser provides pulses of 8 ns duration at 266 nm, with pulse energy 30 mj, spectrometer and CCD As a detector. The emission is observed at a 90°angle to the laser pulse. Has been stated as shown in Figure 1. The recorded spectra of the samples were analyzed using NIST data.

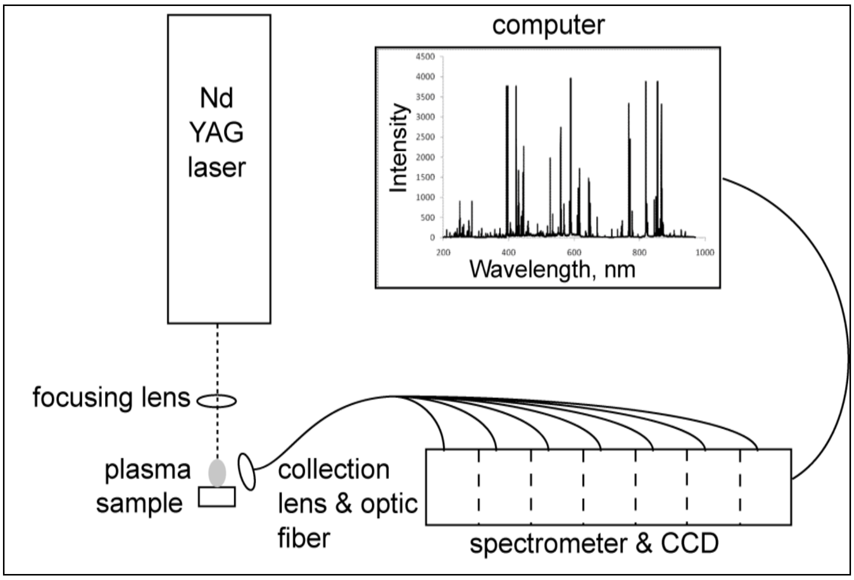

Fig 1: Schematic diagram of the LIBS setup

Software

Origin Lab is software that specializes in data analysis and processing LIBS results for all samples treated by Origin pro 9 Software.

Results and Discussions

Qualitative results

The LIBS emission spectra for the four cement samples (Atbara, Barber, Mas and Sakhar AL Sudan) respectively, shown in Figures from (2 to 5) after irradiation with 30 mJ pulse energy, the spectra were recorded in the region from (200 nm to 650) nm.

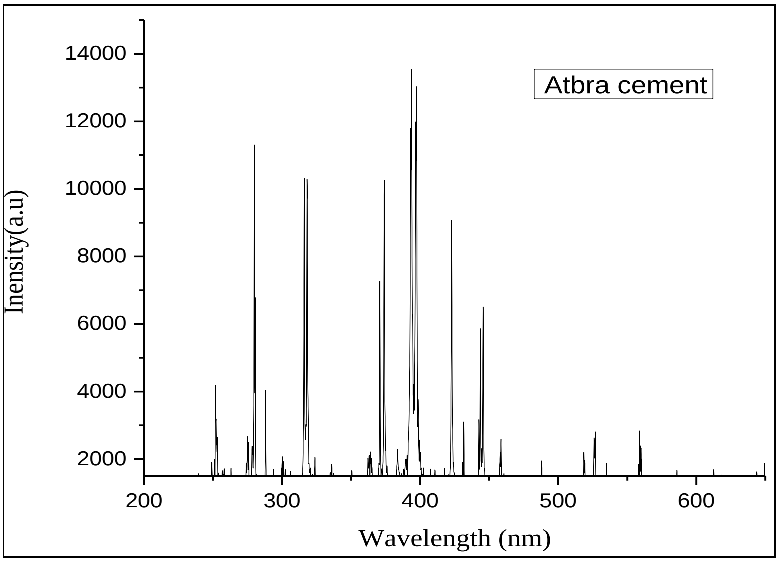

Fig 2: LIBS emission spectrum of Atbara cement

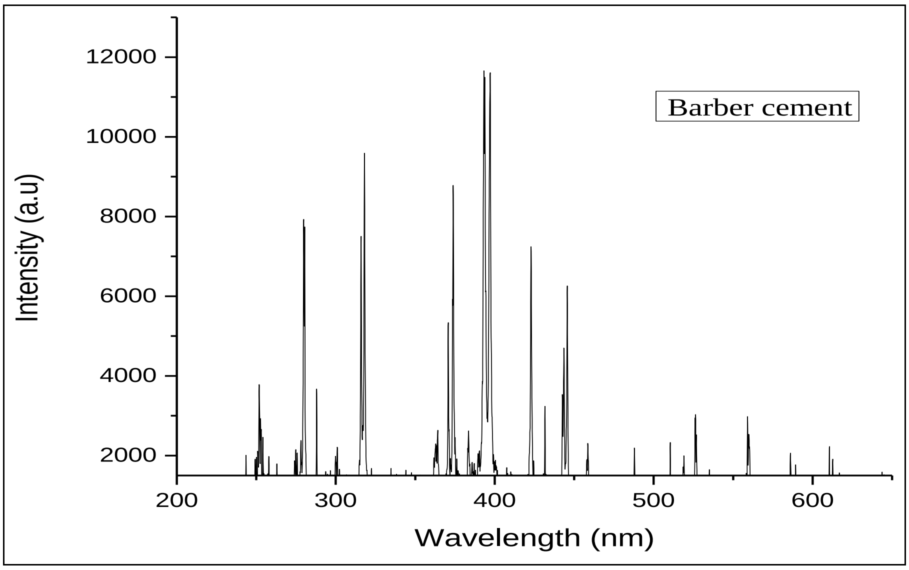

Fig 3: LIBS emission spectrum of Barber cement

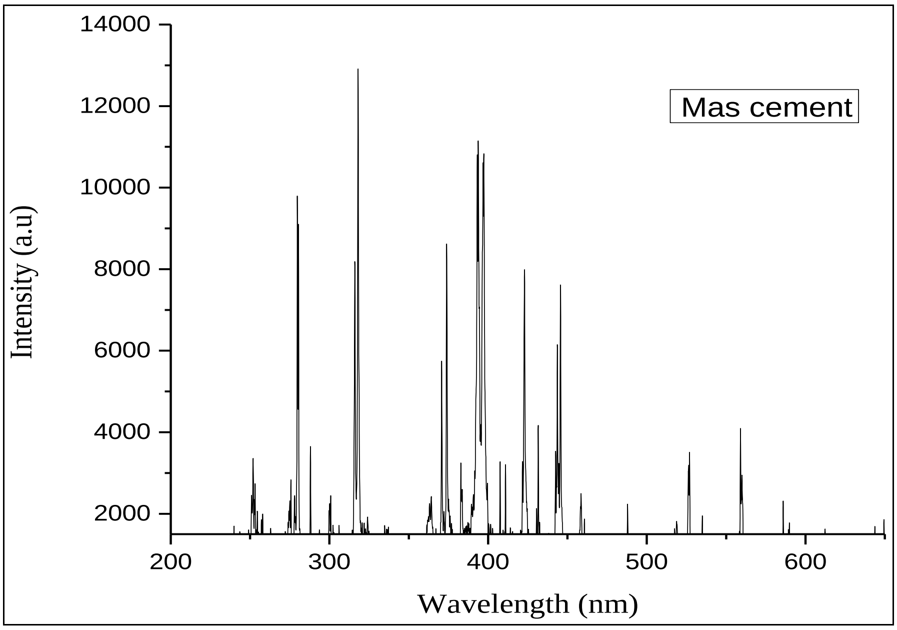

Fig 4: LIBS emission spectrum of Mas cement

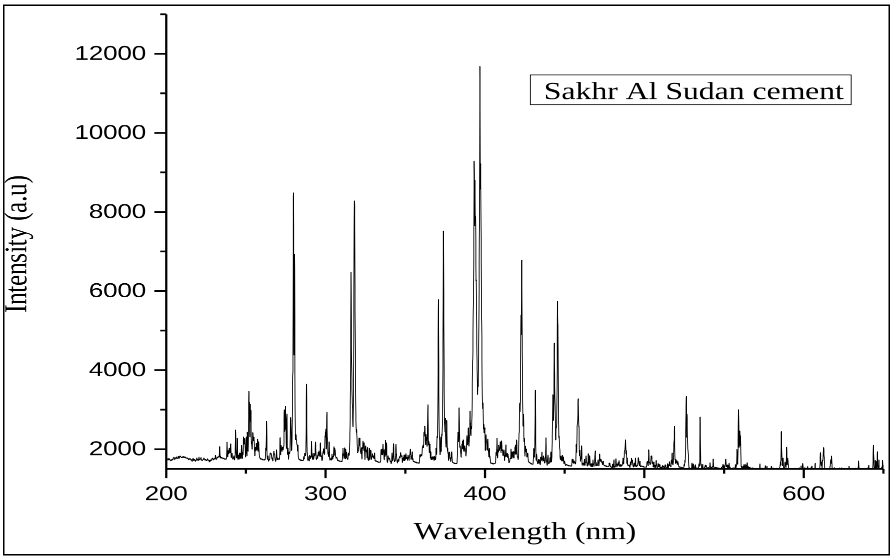

Fig 5: LIBS emission spectrum of Sakhr AL Sudan cement

Neutral atoms Like (Ca, Fe, Si, Na, Ti, Cr, V, Sr, Zr, Kr, K and Cs) that were detected from the analysis of samples spectra. that were found in all samples. In addition to the ions: (Ca^{+1}, Fe^{+}, Si^{+1}, Na^{+1}, Ti^{+1}, Cr^{+1}, and K^{+1}).

The heavy metals like: metals (Cr, Fe, Ti, Mn, V, Xe, Y and Zn) were appeared in the four samples.

Relation between LIBS intensity and laser energy

To find out the relationship between the intensity of LIBS and laser energy, MAS cement was used at different laser energies (10, 15, 20, 25, 30 and 32) mj. The emission spectra was recorded in the (400- 435) nm region at (10, 15, 20, 25, 30, and 32) mJ. At 200ns delay time. The Spectra of this sample were recorded as shown in figure (6). When analyzing the recorded spectra and determining the spectral lines, different elements appeared, such as (Ca, Fe, Si, S, Ti, Cr, Zr, Kr, Y, Xe). Chromium (Cr) was used to clarify the relationship between the energy of the pulsed laser and the intensity of the LIBS signal, as in Figure (7). From Figure 7, it is clear that the LIBS signal is directly proportional to the laser energy. High laser energy produces thick plasma, so the saturation region is predicted at higher laser energies. [13].

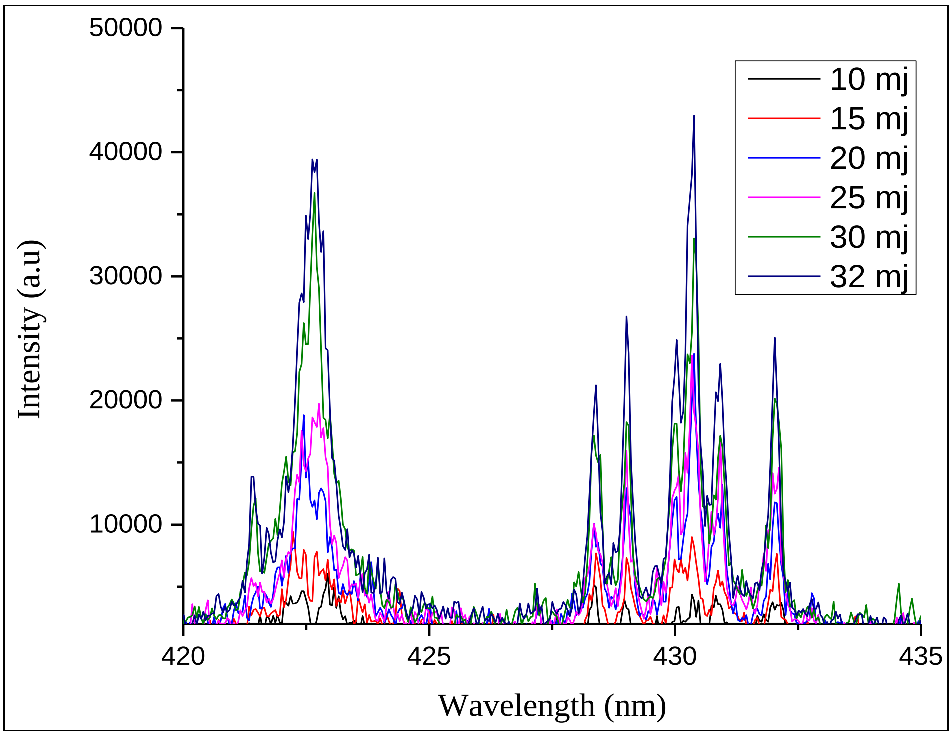

Fig 6: Variation of laser energies with LIBS signal intensity

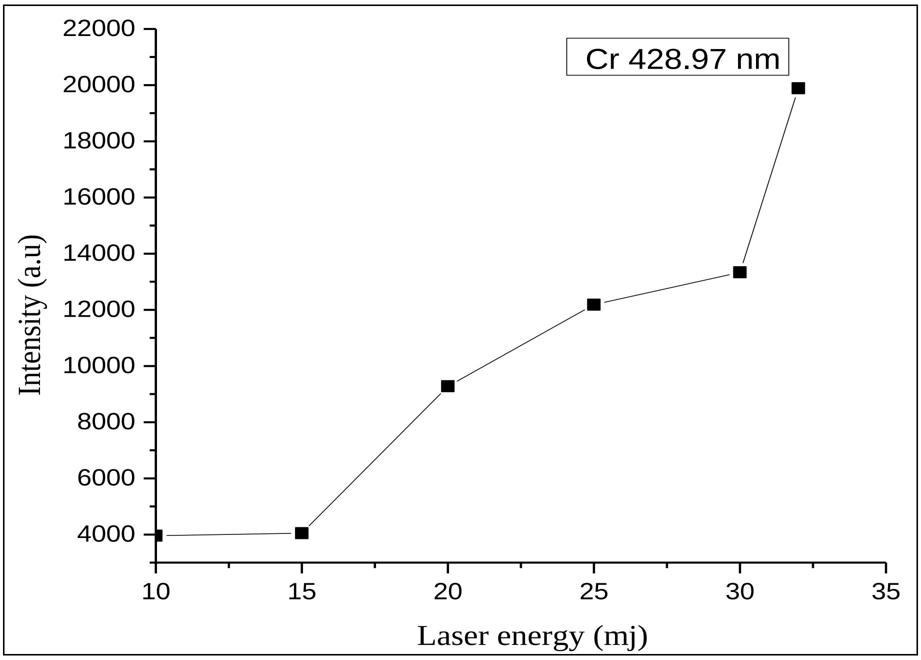

Fig 7: Variation of laser energies with LIBS signal intensity by Cr 428.97 nm

Plasma parameters

Plasma temperature

The chromium lines in the spectral region (428.97, 430.117, 435.17 and 435.96) nm were used to determine the plasma temperature by using the Boltzmann equations.

To obtain high accuracy, LIBS technology is used by selecting spectral lines of chromium element in the region the (428.97, 430.117, 435.17, and 435.96) nm. The spectra were recorded with a 200 ns delay time The plasma temperature was calculated at (10, 20, 25 and 30) mJ laser pulse energy. Table 1 shows the spectral constants of the chromium lines. Using standard equations and well resolved spectral lines in the (428.97, 430.117, 435.17, and 435.96) nm region and was found to be (34987.6K, 119799.4 K, 127178.6 K and 811971.2 K) respectively. Table 2 shows the plasma temperatures obtained from the calculations. Figure (8) illustrate the relation between laser energy and plasma temperature.

Table 1: spectral constants of the chromium lines

Wavelength(nm)	A_{ki}*10^8	g_i	g_k	E_i(ev)	E_k(ev)
428.97	0.316	7	5	00	2.889
430.117	0.26	11	9	3.449	6.33
435.17	0.12	9	11	1.03	3.878
435.96	0.054	5	5	0.983	3.826

Table 2: plasma temperature at different laser energy

Laser energy	10mj	20mj	25mj	30mj
Plasma temperature	34987.6K	119799.4K	127178.6K	881197.2K

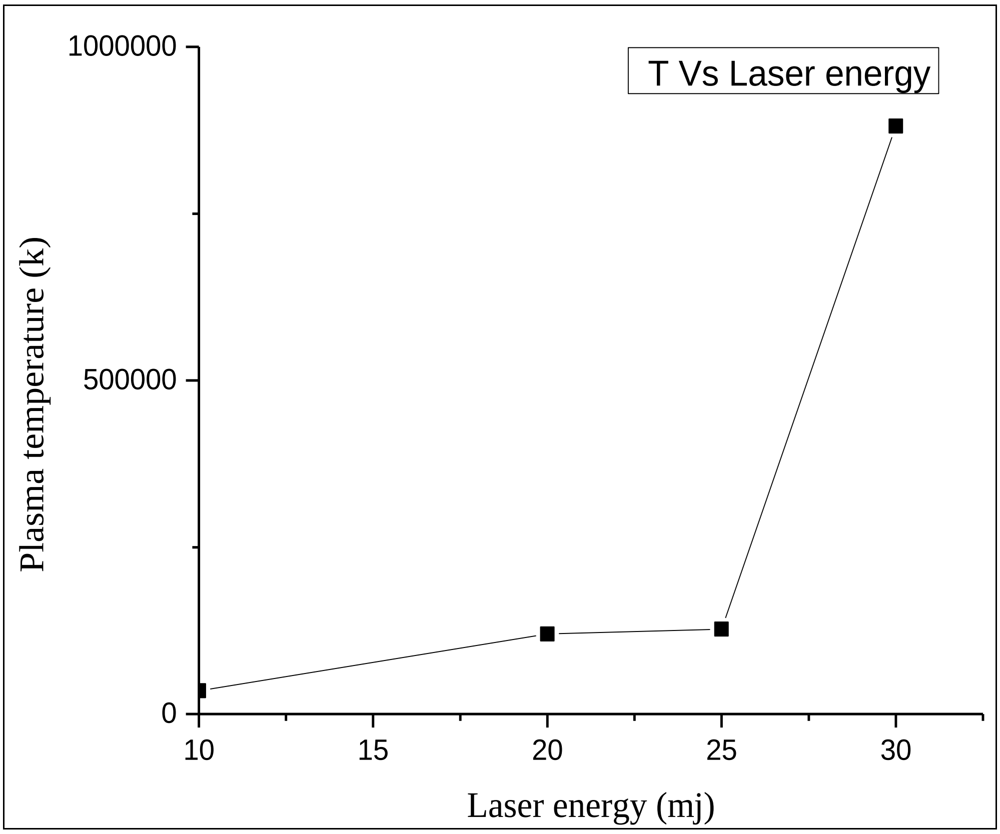

Fig 8: Plasma temperature of Cr versus laser Pulse energy

Electron density

The electron densities for Cr lines for Mas sample were calculated using equation (1):

$$N_e = 1.6 * 10^{12} \Delta E^3 T_e^{\frac{1}{2}} \quad (1)$$

ΔE ≡≡ the largest observed transition energy. T_e ≡≡ excitation temperature (K) [13]. The electron density and plasma temperature at laser pulse energy of (10, 20, 25 and 30) mJ are given in Table below at 200ns delay time.

Table 3

Laser pulse energy (mj)	Plasma temperature (K)	Electron density(cm^{-3}) (Cr at 428.97nm)	Electron density (cm^{-3}) Cr at 430.117nm	Electron density (cm^{-3}) Cr at 435.17nm	Electron density (cm^{-3}) Cr at 435.96nm
10	34987.6	$0.722*10^{16}$	$0.715*10^{16}$	$0.691*10^{16}$	$0.687*10^{16}$
20	119799.4	$1.33*10^{16}$	$1.32*10^{16}$	$1.279*10^{16}$	$1.27*10^{16}$
25	127178.6	$1.37*10^{16}$	$1.36*10^{16}$	$1.318*10^{16}$	$1.3*10^{16}$
30	811971.2	$3.47*10^{16}$	$3.44*10^{16}$	$3.33*10^{16}$	$3.31*10^{16}$

Conclusion

LIBS is used to determine the composition of the Sudanese cement samples. The emission spectra presence of heavy metals (Cr, Fe, Ti, Mn, Sr,V, Xe, Y and Zn) in addition to other elements (Ca, Si, S, Zr, Kr and Na) in cement samples. The laser pulse energy is directly proportional to the intensity of the LIBS signal. From calculations the electron density is also increased with increase in laser pulse energy.

Recommendations

1. Using the LIBS technique to calculate the concentrations of the elements in all samples.
2. Analysis of other types of Sudanese cements using libs technique.
3. Using XRF technology and comparing its results with LIBS technology.
4. Using an excimer laser in the analysis and comparing its results with those of libs.
5. Identify the relationship between the delay time and laser energy.

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