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Laser-induced breakdown spectroscopy (LIBS) technique for the characterization of Iraqi cement

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In this study, qualitative and quantitative values of different Iraqi cements have been estimated using laser-induced breakdown spectroscopy (LIBS), which provides a sensitive elemental analysis based on the measurement of plasma lines that generated after laser interaction at a sample. A passively Q- switched Nd: YAG laser operating at wavelength of 1064 nm, energy of 100 mJ, and pulses of 9 ns pulse width was applied as a radiation source. In addition, Iraqi Portland cement samples produced in Kufa and Mass factories have been examined using EDX for determination of major and minor elements concentration such as Ca, Si, Al ,Fe and Mg. LIBS spectra of different samples were recorded from (320 - 740) nm spectral range. The line intensities of these elements are identified and marked, the possibility to carry out a quantitative analysis using the LIBS technique was checked through the comparison the obtained result with related EDX data. For quantitative measurements, the concentrations of different elements in the cement are estimated by construction calibration curves and analysis signals of high purity standard samples as a first researchers work on it as our best knowledge.

Keywords: Laser-induced breakdown spectroscopy (LIBS); Passively Q-switched Nd: YAG laser; EDX; Cement.

1. INTRODUCTION

Ordinary cement is a water-based binder used to bind other building materials together. Every year a huge amount of cement produced and used for the construction of building, roads and highways, and other local purpose [1]. Using bad quality cement in structural and constructional works may cause loss of people lives and properties. The choice of cement type involves the correct knowledge of the cement ingredients. Even a small variation in the chemical composition or physical state of cement could cause substantial variations in its performance [2, 3]. For these reasons, measuring the concentration of major and minor elements is necessary to differentiate the different kinds of cement for quality control. Nowadays, complete analysis of cement can be done through different methods such as wet chemical analysis and costly instrumental measurements. In cement Factories, X-ray fluorescence (XRF) is widely used for characterizing the elemental composition. Although XRF technique is fast and accurate cement analysis, but it needs expensive apparatus and unsuitable for analysis of very light elements e.g. H to Ne. [4-6]. On the other hand, analysis using chemical methods such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectroscopy (AAS) suffer from disadvantages that it requires sample preparation and time consuming for sample to be dissolved [7]. In the last decade, Laser-Induced Breakdown Spectroscopy (LIBS) has become a popular analytical method for its unique features such as little sample preparation, applicability to any type of sample [8] and remote sensing capability [9]. LIBS has been used in construction industries for determination of chloride content in different types of cement [10] and in situ analytical assessment of historical buildings [11]. This method offers multi-elemental and fast measurement detection capability under ambient and harsh conditions and it is employed for in situ and remote monitoring in industrial processes [12].

The physical nature of the LIBS technique stems from the generation of high temperature plasma, induced by a short laser pulse (typically some nanoseconds and ten to hundreds of mille-Joules per pulse) [13]. When the laser pulse impacts the surface of the sample a small number of elements is ablated from the surface and interacting to form high energetic and hot plasma that contains free electrons, excited atoms and ions. The emitted light from the plasma is analyzed and the elements present in the sample are determined through their unique spectral lines [14]. Beside this qualitative analysis, the quantitative elemental composition analysis of material can be obtained by the preparation of linear calibration curves using several standard samples [15].

In this study, LIBS data were recorded and analyzed in order to identify the compositional difference for three different types of cements that are usually used in Iraq. The obtained results were compared with EDX analysis results for the same samples.

2. EXPERIMENTAL PROCEDURE

2.1. LIBS system

The experimental set up used for LIBS analysis of cement samples is shown in Figure. 1. Samples were irradiated by nanosecond Q-switched Nd: YAG laser operating at wavelength of 1064 nm, pulse width of 9 ns, output pulse energy was 100 mJ. The laser beam is focused by a convex lens with focal length of 100 mm on the sample surface. The diameter of the focused laser spot is 1.0 mm and the laser power density is in the order of 14.2*109 W/cm2 which is enough to induced ionization and generates plasma on sample surface.

The emission of plasma was collected by a imaging lens with diameter of 15 mm, and focused onto optical fiber type (SMA, 50 um/0.22 NA), which deliver the plasma light to the entrance slit of spectrum analyzer model (CCS-100) with (1200 Line/ mm) grating and slit dimension of 20 um. The grating disperses light according to wavelength and then reflected by mirrors to detect and convert optical signals to digital, and then moves the digital signal to the application.

Each emission spectrum obtained by integration of 10 laser shots impinging on surface of the sample. Specific software was utilized to illustrate the data as a diagram between intensity and wavelength. The experiment is performed under fixed environment conditions.

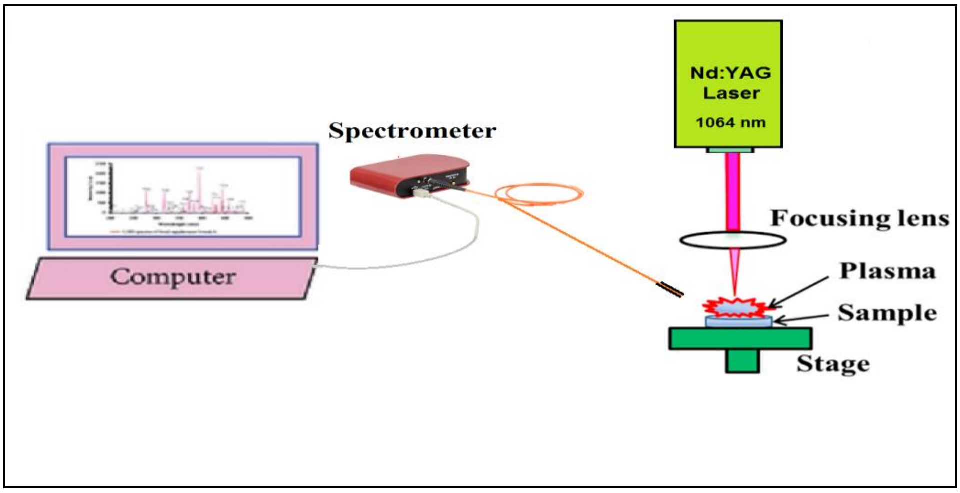

Figure.1: Experimental set up for LIBS Measurements

2.2. Preparation of experimental samples

There are several brands of cement available at Iraqi market their chemical compositions are same. Variations in physical properties occur due to the variation of constituents. In this study, three different types of cement are Ordinary Portland cement Mass plant (OPC) type CEM I 42.5 R used in general construction, Sulfate resistance cement Mass plant (SRC) for civil construction, that needs high sulfate resistance especially for foundations and resistance Portland cement from Kufa plant have been used.

A pressed powder pellet is prepared from 3.0 gram for each type of cement. Hydraulic pressure machine model (Auto Series) is used to press powder cement without binder at (7.0 ton) to a disc of 1.0 cm diameter and 5.0 mm thickness as shown in Figure. 2.

Figure. 2: Experimental pressed cement samples

2.3 Energy-dispersive X-ray (EDX)

To conduct elemental composition of cement samples, Energy-dispersive X-ray (EDX) microanalysis model (EFI Bruker) has been used. EDX relies on the investigation of an interaction of some source of X-ray excitation and a sample [16]. By measuring characteristic X-rays that are emitted, it is possible to distinguish the elemental compositions on the sample surface. The major and minor elements present in cement sample were identified; their concentrations that measured by EDX are used to prepare the calibration curves. In cement analysis Ca, Si, Al, Fe and Mg are expressed as the (CaO oxides form, SiO_2, Al_2O_3, Fe_2O_3 and MgO). These oxides eventually become more complex with compounds responsible for main cement properties such as early strength, set times and color effects [17]. The obtained EDX results are finally compared with related LIBS data.

2.4 Calibration Curves

The calibration curves were constructed based on EDX results. Known concentrations of Ca, Si, Mg, Al, Fe metals were used. These metals were in powder form with high purity 99.99% provided from HiMedia. Five groups of stoichiometric alloys comprising these metals are prepared, Pb powder with the high purity (99%) was chosen as a matrix for all alloys. The first group constructed from pure calcium and different combined concentrations Ca and Pb. The percentage of calcium was (10, 20, 30 and 40) % respectively. Other groups of alloys are made using the same procedure as listed in Table. 1

Table 1 Concentration of elements in prepared alloys

Sample Metal	S1 (%)	S2 (%)	S3 (%)	S4 (%)
Ca	20	30	40	100
Si	10	20	40	100
Mg	1	5	10	100
Al	1	5	20	100
Fe	1	5	10	100

All samples are weighed using a sensitive digital balance, and then each combination was mixed very well for one hour in the electric mixer (Mini Mill II), which is utilized to homogenize the mixture. The mixed combinations are pressed to the same size discs of 10.0 mm diameter and 5.0 mm thickness.

3. RESULT AND DISCUSSION

3.1. Qualitative analysis

LIBS emission spectra of the pellets made from Ordinary Mass, Resistance Mass and Resistance Kufa cement samples were recorded at the spectral range (320-740) nm as shown in Figure. 3. The characteristic emission lines of main elements are observed in all cement samples but in different intensities, these elements are identified and marked in the figure. The interference free lines with high signal to noise ratio are chosen at specific wavelengths. The detected elements ordered from highest to lowest intensity were: Calcium Ca at (430.4) nm, Silicon Si at (390.5) nm, Aluminum Al at (394.4) nm, Magnesium Mg at (518.5) nm and Iron Fe at (445.6) nm. These spectral lines experimentally observed in LIBS spectra from pure

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metals pellets, all elements present in the samples recorded using the database given at the National Institute of Standards and Technology (NIST) atomic spectra database [18].

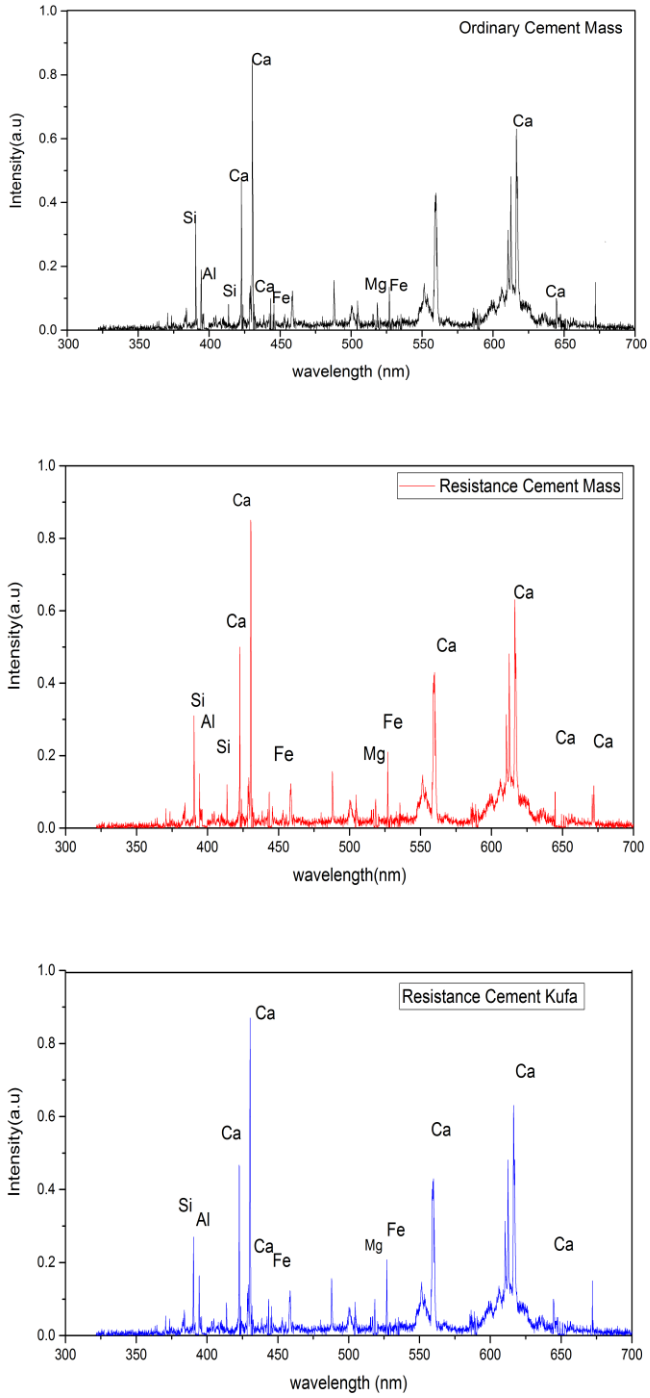

Figure 3 Typical LIBS spectra for ordinary, resistance Mass and resistance Kufa cement samples.

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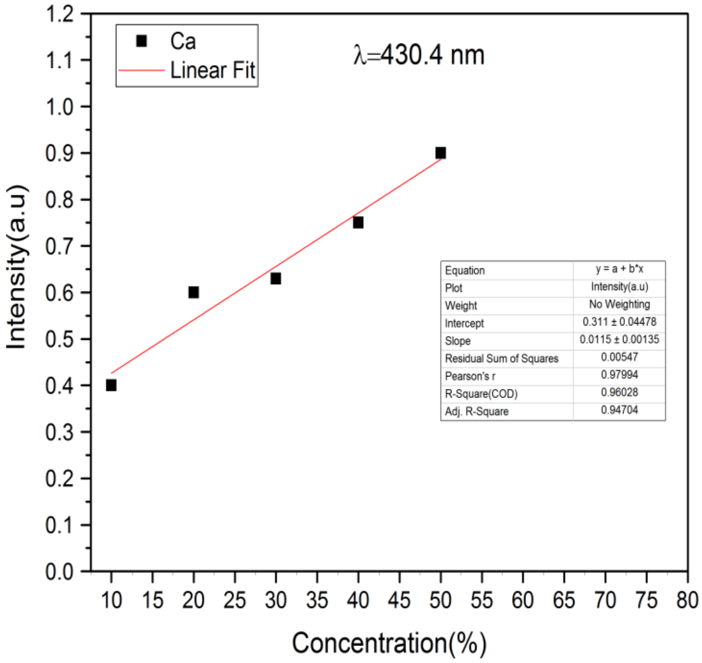
3.2 Quantitative analysis

For quantitative analysis, calibration curves are prepared for all above-mentioned elements present in cement samples. High purity metals samples and alloys comprising these metals with lead Pb are used. To examine the homogeneity of these alloys, LIBS spectra at different locations on the surface of samples have been captured and observed. The atomic line intensities were almost same due to good alloys prepared. The intensity of spectral lines at selected wavelengths was highly correlated to metal concentrations [8]. In other words, the low concentration displayed a low peak of intensity, and vice versa. The calibration (standard) curves plotted between elemental concentration and emission line intensities of these elements as shown in Figure. 4. There is a significant linearity accuracy of measurement enable the unknown concentrations of interesting metals to be measured. The slopes of calibration curves were calculated from fitting data in linear regression functions for these spectral lines. LIBS spectra of cements standard samples are recorded at the same experimental conditions; consequently, the percentage of major elements in all cement samples is calculated from these calibration curves. The analytical results of all elements in cement samples show that all samples consisted of Ca as the highest concentration element with ratio (40-50) % of total cement content. The concentrations of the other elements obtained using LIBS varied from (10.1-9.2)% for Si, (2.12-2.95)%for Al, (1.408-1.93)% for Mg and (2.423-4.08) % for Fe, Significant agreement is observed in element concentration given by EDX analysis.



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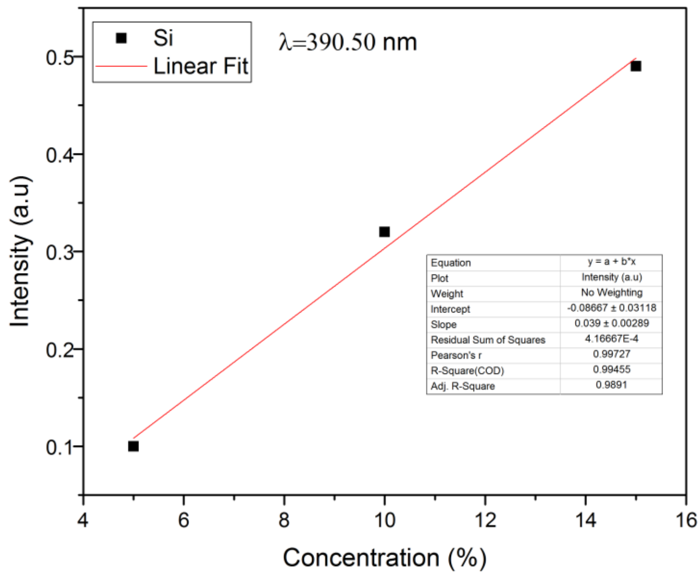

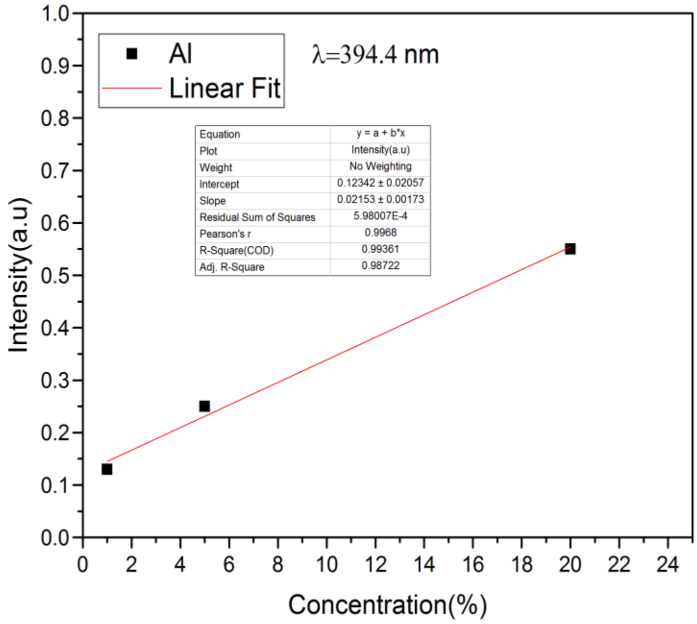

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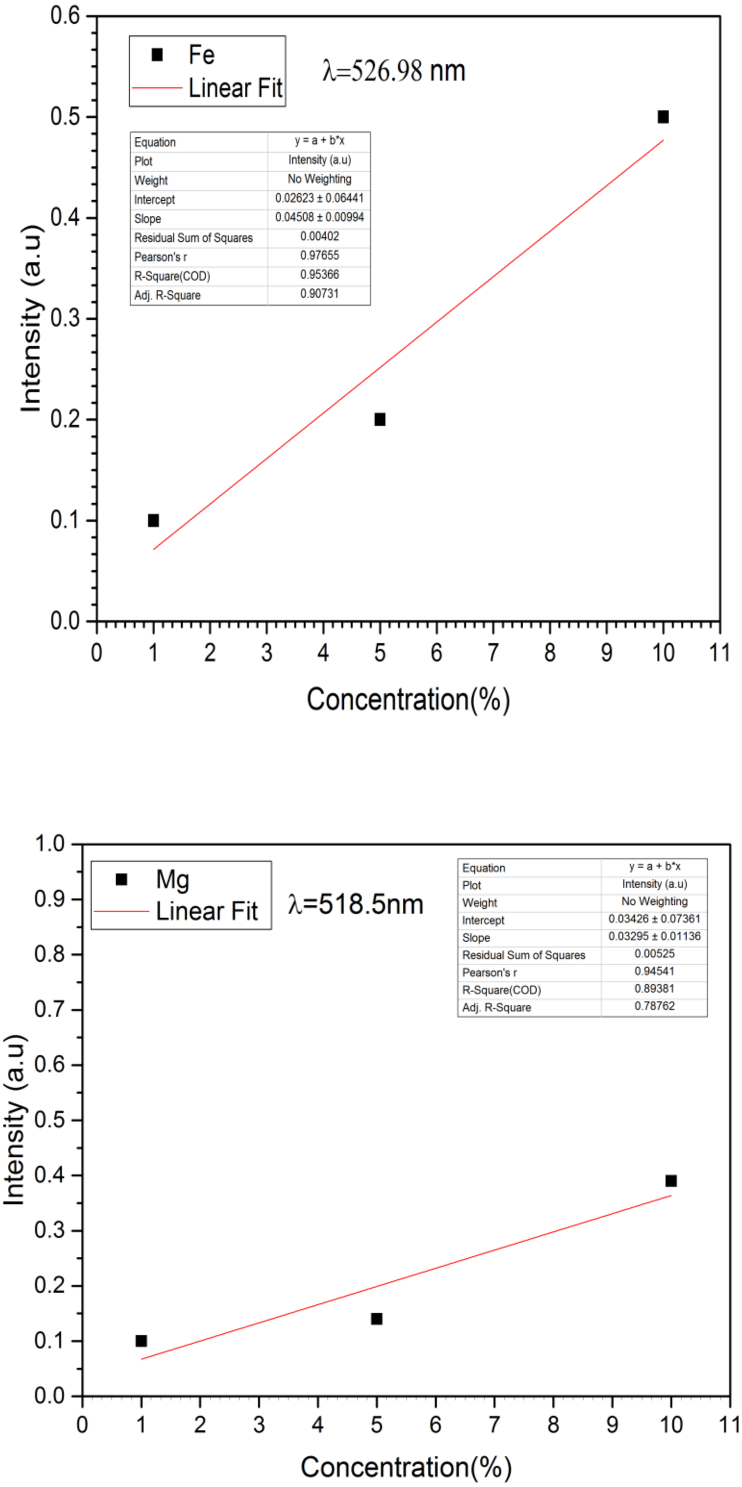
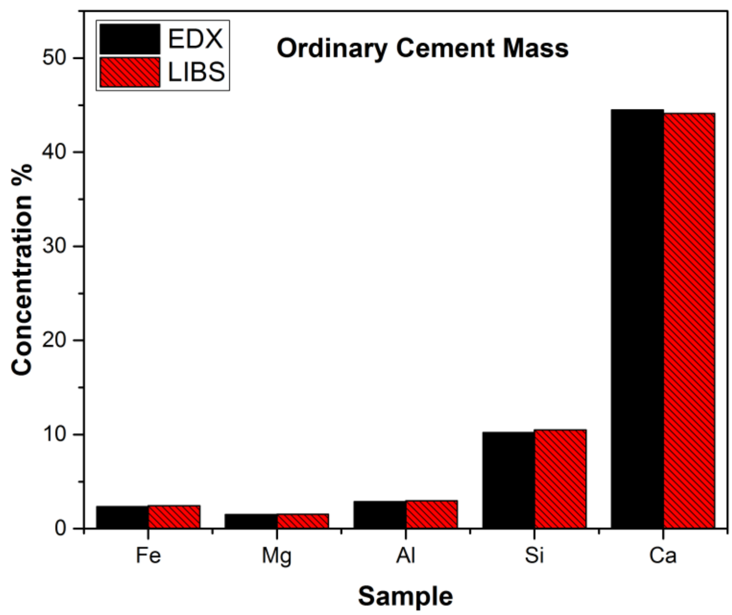


Figure. 4: Calibration curves for Ca, Si, Fe, Al and Mg

Figure. 5 shows the bar diagram of quantitative analysis determine by LIBS and for comparison the results from EDX. The same trends in the relative changes of element concentrations from

Kufa and Mass cement are noticed in both techniques**,** however, the analytical results are not completely corresponding for each other. In LIBS, the interaction between the laser and the sample is influenced significantly by the overall sample composition, so that the intensity of the emission lines observed is a function of both the concentration of the elements of interest and the properties of the matrix that contains them. Table 2 summarizes the measurement percentage errors from LIBS method with respect to those results obtained from EDX analysis. This encouraging results support LIBS as a promising solution to replace the present conventional methods in quantitative analysis of elements.

It is notes that the measured concentration values of detected elements in all three cement samples are different, which may be attributed to the raw materials being used for the production of Iraqi cement. However, the amount of (CaO SiO2, Al2O3, Fe2O3 and MgO) oxides were found within Iraqi standards specifications limits [19]. On the other hand, the concentration of Al for the ordinary Mass cement was found to be higher than the resistance cement. Besides, the measured concentration of Fe for ordinary Mass cement was less than resistance cement. These variations could reduce risk of sulfate interaction making resistance cement more durable than ordinary cement in rich sulfate environment. Since higher MgO content may cause expansion cracks known as magnesia expansions [20], so specify the amount of MgO cement should be not more than 2.0 %, it is found all cement sample were within the specified limits.



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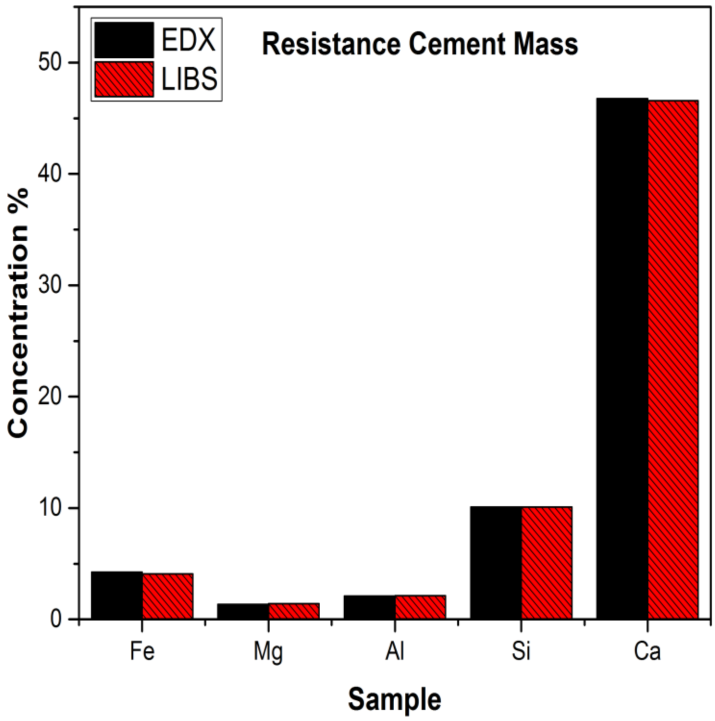

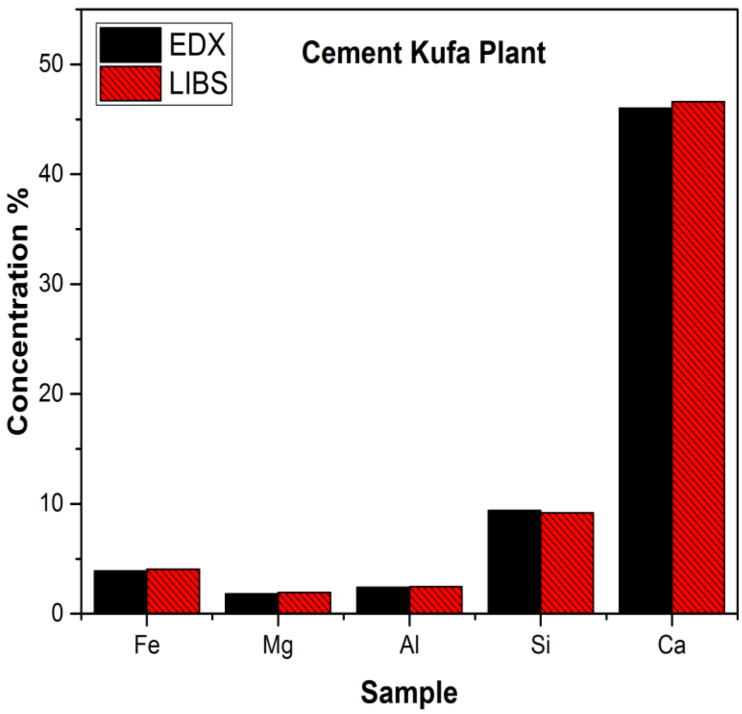

Figure 5 Comparative Bar charts of ordinary, resistance Mass and resistance Kufa cements elements concentrations ratio determined by EDX and LIBS

Table 2 The measurement errors from the LIBS method compared with traditional EDX analysis

Cement / Element	Ordinary Mass	Resistance Mass	Resistance Kufa
Mg	3.02%	3.10%	3.50%
Fe	3.05%	3.12%	3.40%
Al	2.10%	1.43%	2.92%
Si	1.94%	1.10%	1.15%
Ca	0.86%	0.36%	0.86%

4. CONCLUSIONS

The applicability of used laser-induced breakdown spectroscopy (LIBS) as a new procedure for compositional analysis of Iraqi cement has been tested. Qualitative and quantitative measurements for elemental detection have been investigated for three samples of Kufa and Mass Factory based on emission spectral data. The sensitive spectral lines of Ca, Fe, Mg, Al and Si elements in all samples were identified according to NIST standard data. The calibration curves were highly correlated and effective in quantifying the major metals concentration in samples. The method was found to meet the ASTM requirements in accuracy for the analysis of cement samples and to be comparable with EDX method in real sample analysis. Beside the multi elements analysis, the potential benefits of this technique include, that sample analysis cost by LIBS is low as compared to other conventional analytical techniques and can analyze large number of samples in shorts time**.**

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