Original article

Characterization of *Adansonia digitata* using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract

In this work, two samples of *Adansonia digitata*. (Baobab) have been conducted using laser induced breakdown spectroscopy techniques. Nitrogen pulse laser 337.1nm with 100, 200 and 400mJ and pulse duration 10 ns was used as irradiation source. Considerable number of elements have been detected in the two samples e. g. Ca^{+2}, Fe^{+2}, Cr^{+2}, P^{+2}, Hg^{+2} and Mn^{+2}. Some of these elements are considered to be beneficial if used in low concentrations while others are doomed to be toxic such as: Hg^{+2}. More studies to calculate the concentrations of these elements were suggested.

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Introduction

Africa has an abundant novel plant species which are known to be rich in health-promoting compounds, many of which remain undiscovered or unused by the western society. The Baobab *(Adansonia digitata.)* is widely distributed throughout the sub- Saharan Africa and Western Madagascar areas and has many uses, such as medicine, food, and beverages (Woodborne, 2015). *Adansonia* species comprises 8 different species with large, spectacular, nocturnal flowers (Wickens, and Low, 2008). One of these species is the *A. digitata*. The other is restricted to North-Western Australia (*A. gibbosa*), and the remaining six species are endemic to Madagascar. African baobab is regarded as the "Queen of all carbon storage trees". It is very long-lived tree. It is thought to be older than 1000 years. Every part of the Baobab tree is reported to be useful. A point in case, the trunk of the tree swells greatly during rainy season and absorbs 1000 liters of water. As of having Baobab tree an extensive root and high water holding capacity, it can tolerate well high temperatures up to 40–42°C (in West Africa), it's resistant to fire, and survive low temperature as long as there is no frost. The fruit of *Adansonia* is said to have high vitamin C content 10 times that of an orange, while leaves are high in mineral content and pro-vitamin A. the oils extracted from the seeds are said to be edible due to the fatty acid composition. Knowledge of all this properties is limited due to the consumers and researchers (Zahra'u *et al.*, 2014).

Laser induced breakdown spectroscopy offers a promising new effective technique for both qualitative and quantitative analysis of various materials in all aggregates states (David and Radziemski, 2006). LIBS utilizes an intense laser pulse to determine the atomic or the elemental composition of a sample via generation of a high-temperature micro-plasma followed by time-resolved spectroscopy (Rehse, 2012).

For Plasma generation, there is threshold value of the energy density. The threshold value depends on the absorption coefficient of the sample surface of the laser wavelength, which is highly different by the sample phase. For instance, gas and liquid need more energy to make breakdown. Solids with a dark color surface easily make a strong breakdown compared to clear or highly reflective solids.

Several types of pulse laser were used to make laser-induced Plasma. An Excimer laser was an important pulse laser especially for the UV light pulse. XeClexcimer with 308nm was used in the LIBS to measure the elemental distribution on the paper coating. The laser energy of 0.2mJ was focused and made a crater of 30 micro-meter diameter. More than 90% of ingredients in the paper coating are pigment, binder and other agents. Several types of pulse laser were used to make laser-induced breakdown Plasma. An Eximer laser was an important pulse laser especially for the UV light pulse. XeCleximer with 308 nm was used in the LIBS to measure the elemental distribution on the paper coating. The laser energy of 0.2 mJ was focused and made a crater of 30 diameter. More than 90 % of ingredients in the paper coating are pigment, binder and other agents. A typical Nitrogen laser has wavelength 337.1nm and pulse duration of 10ns. Just like the Excimer laser, the laser beam is usually a few cm wide, so a tight focusing is needed. The surface of solar cell was measured by Nitrogen laser breakdown and only a 40nm thick Ti O_2 layer was detected (Kim, and Lin, 2012).

Researchers have used double or multiple pulses for LIBS, in various configurations, because it results in very large enhancements in signal intensities. Femto-second laser pulses for ablation and LIBS plasma initiation have advantages. The pulse energy is deposited before the plasma is generated, eliminating shielding effects. The laser interaction with the surface is primarily through depth, not through spreading out due to heat conduction. But the fact that the plasma starts after the laser–material interaction leads to shorter-lived plasma of lower temperature, hence a lower intensity. Pinon and Anglos (2009) studied and compared single and collinear double-pulsed 450 fsec plasmas on brass, as a function of the delay between the two pulses. They are found, in the duplicate process case “DP”, a signal enhancement of almost an order of magnitude over the single process case “ SP”, when the SP energy is equally divided over the two pulses. With an inter pulse delay of 50–1000 ps, a higher signal reproducibility, higher plasma temperature, and longer plasma lifetime was observed. A byproduct was plasma initiation at a lower influence, which minimizes surface damage on sensitive substrates and provides better spatial resolution (David, and Radziemski, 2006).

When the laser pulse is directed to the sample, apportion of the sample in the focal volume would be atomized. Consequently, plasma would be produced which excites and re-excites the atoms to emit light. The interaction between the laser beam and the material is a complicated process dependent on many characteristics of both the laser and the target material. A measurement of the wavelengths and the intensities of the observed emission lines can be made if the emitted light is collected and recorded (Kim, and Lin, 2012).

The use of LIBS for elemental analysis relies on some fundamental assumptions that must be verified, especially when semi-quantitative and quantitative analysis of samples is pursued. First of all the conditions of optically thin plasma and LTE are always the underlying premises for laser induced plasma studies by emission spectroscopy, both for fundamental studies and for analytical applications. Secondly, any kind of substance can be analyzed by LIBS with no sample pretreatment and no particular sampling procedures needed. Thus, the analysis can be performed in air, in vacuum, in fluids, and even under extreme conditions such as high temperature and pressure environments. What renders the range of applicability of LIBS so wide are primarily its several advantages, particularly its extremely flexible experimental set-up (Gaudiuso, 2010).

LIBS is useful in a wide range of fields, namely, those which can benefit from a quick chemical analysis at the atomic level and without sample preparation (Anabitarte *et al*. 2012). The ability of LIBS to provide rapid multi elemental microanalysis of bulk samples (solid, liquid, gas, and aerosol) in the parts-per-million (ppm) range with little or no sample preparation has been widely demonstrated in the environmental and medical sciences. LIBS is continuously being applied for new purposes that involve helping answer questions in astronomy, archeology and forensics (Grissino-Mayer, and Martin, 2015). LIBS is also applicable to the analysis of extremely hard materials that are difficult to digest or dissolve, such as ceramics and semi or super-conductors. Its capability for simultaneous multi-element determination, localized microanalysis, and surface analysis are also of great importance and it has been used successfully in hazardous and difficult environmental conditions to study remotely located samples for online and real time information about their spectra. Additionally, the analysis process is fast these features make laser induced breakdown spectroscopy unique (Rehse, 2012).

LIBS has been applied in 2008 by Vincent Juve, *et al* to analyze trace elements contained in fresh vegetables. A quadrupled Nd: YAG laser is used in the experiments for ablation. Additionally, frequently consumed vegetable samples that come from local markets such as potato is also used. The spectral analysis of the plasma emission reveals more than 400 lines emitted by 27 elements and 2 molecules, C_2 and CN. Trace as well as ultra-trace could be found among these species. Subsequently, a space resolved analysis of several trace elements is applied to typical root, stem and fruit vegetables, the results from this study demonstrated the potentials for botanical and agricultural studies as well for food quality or safety and environment pollution assessment and control (Juvé *et al.* 2008).

Jidong Lu *et al.*(2009) have used laser induced breakdown spectroscopy (LIBS) to improve the precision of the elemental analysis of coal Organic components such as C, H, O, N and inorganic components such as Ca^{+2}, Mg^{+2}, Fe^{+2}, Al^{+2}, Si^{+2}, Ti^{2+}, Na^{+}, and K^{+}. The dependences of the relative standard deviation (RSD) of the LIBS measurements on the experimental parameters including the sample preparation parameters, lens to sample distance, sample operation mode, and ambient gas have been investigated. The results indicate that the precision of LIBS measurements for the coal sample can be improved by using the optimum experimental parameters (Li *et al*. 2009).

Experimental

Two samples of *A. digitata* (Baobab) in the powder form collected from two different locations Northern Kordofan state and Western Africa) in addition to Laser-induced breakdown spectroscopy set up which consists of Nitrogen laser, optical system (convex quartz lens (f=10cm) and mirror (7.4×4.7cm)), sample container which is made of quartz, optical fiber, detection system (USB2000 Spectrometer) in addition to Computer with ocean optic software and origin9 program. The two samples of *A. digitata* were collected from Northern Kordofan state, Sudan and western Africa. A mesh (2mm) was used to eliminate the big granules and in order to have *A. digitata* powder. Then laser induced breakdown setup “LIBS setup” was prepared and the first sample was placed in the container in front of the laser and the laser energy was set at 100mJ, the laser beam was directed to the mirror, and the reflected beam was collimated and tightly focused on the sample using convex lens to create a breakdown in the sample, the emitted spectra was collected using optical fiber which was connected to USB 2000 spectrometer where the collected data was recorded. The recorded data was analyzed using the national institute of standards and technology (NIST database). Then the laser energy was increased to 200 and then to 400mJ and the emitted spectra was recorded and analyzed for each one. These steps which have been done were repeated and applied to the second sample also.

Results and Discussion

1. Irradiation with 100mJ

Figures (1) and (2) show the emission spectra for the two samples of *Adansonia digitata*, respectively after the irradiation with 100mj. Table (1) illustrates the analyzed data for the two samples.

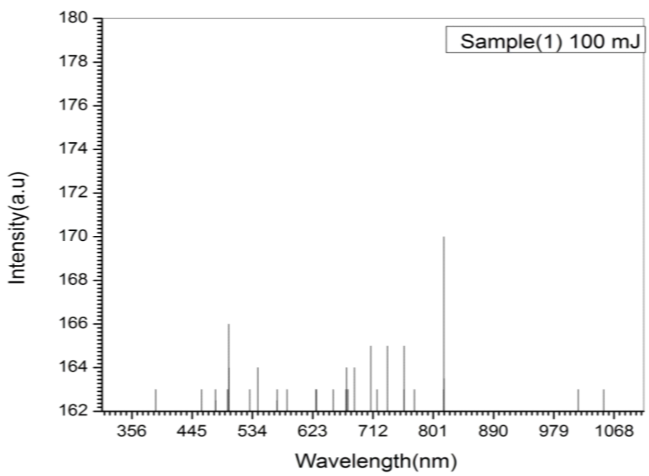

Figure 1. The emission spectra for *Adansonia* collected from Sudan using 100mJ**.**

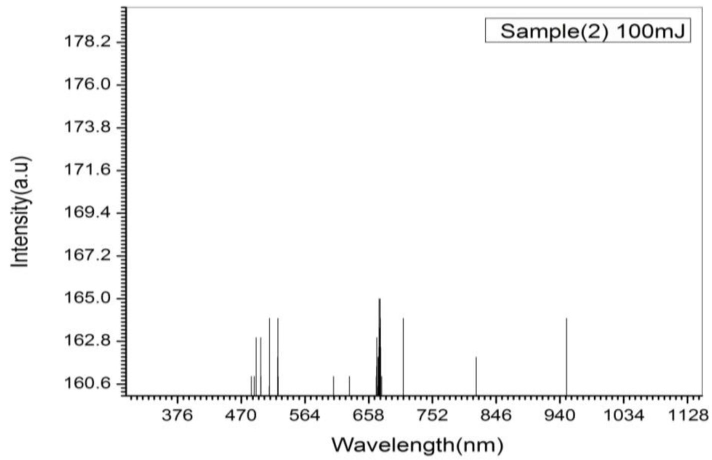

Figure 2. Irradiation spectra of *Adansonia* from Western Africa using 100mJ

2- Irradiation with 200mj:-

The emission spectra of the two samples were recorded as shown in figure (3) and (4), while the analysis of the spectra is displayed in table (2).

Table 1. The analyzed data of *Adansonia* collected from Sudan and Western Africa using 100MJ

Element	Wavelength (nm)	Intensities (a.u)		Element	Wavelength (nm)	Intensities (a.u)	
		S1	S2			S1	S2
AII	677.6938		161.9066	Ho I	674.4834		165.6542
Ar I	672.2755	164.5370		In II	773.7641	163.5438	
Ar II	497.2033	163.5438		Mn II	950.0111		164.5944
	525.1055		163.1084	N I	1053.3464	163.4553	
Ar III	480.1404	163.5438		N II	684.7172	164.5370	
Ba I	6o6.3097		161.7154	Nd II	817.2517		162.6277
Be I	815.8880	170.5009		Ne I	485.2588		161.5242
C I	530.0849	163.5832		O II	733.0619	165.6629	
	671.0842		162.8681	Pr I	653.4352	163.5438	
C II	1014.2439	163.5832		Pu I	709.2313		164.5452
C III	676.1831		162.9609	Rh I	542.5266	164.5370	
Ca III	584.8283	163.4996		Sc I	511.8862		164.6927
Ce I	629.5379		161.5242		626.9522	163.5438	
Cr I	673.8751	164.5370		Tb II	758.1231	165.5302	
Eu I	669.3846		163.4908	Th I	391.0935	163.5438	
Fe I	570.6092	163.5438			498.4781		163.5892
Fe II	458.2786	163.5832		Ti I	488.4692		161.5679
Fr I	628.5519	163.5438		Tm II	672.7838		165.6542
Hf I	459.8782	163.5832		V I	523.4059		164.6927
198 Hg I	708.1786	165.4859			675.2970	163.5832	
Hg I	717.5988	163.6274		W I	498.8029	166.5676	

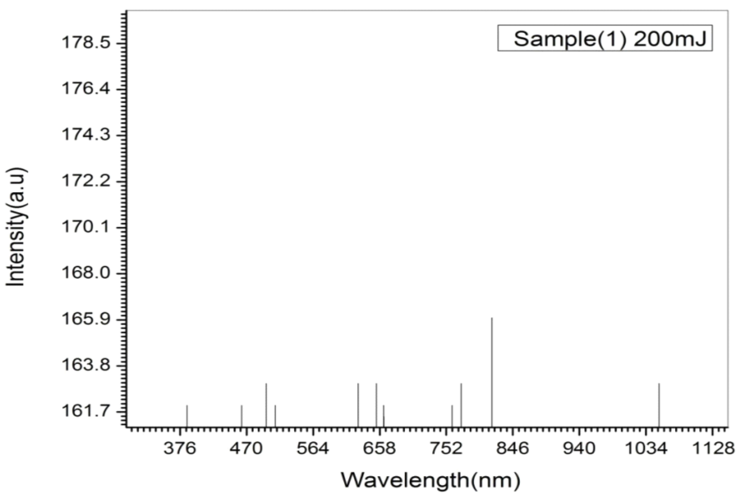

Figure 3. The emission spectra from sample *Adansonia* collected from Sudan using 200mJ.

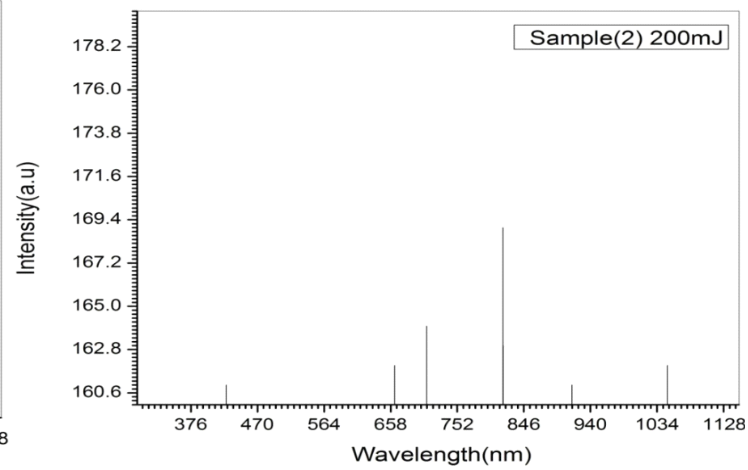

Figure 4. The emission spectra for *Adansonia* collected from Western Africa using 200mJ

Table 2. The analyzed data for *Adansonia* collected from Sudan and Western Africa using 200mJ

Element	Wavelength (nm)	Intensities (a.u)		Element	Wavelength (nm)	Intensities (a.u)	
		S1	S4			S1	S2
Al IV	426.0307	162.6296		Nd II	817.2517	166.6414	169.5438
Ar I	772.3062	163.5845		P I	1052.9327	163.5845	
Ar II	1049.5334		161.5242	Rh I	662.7749	162.6296	162.7206
B II	652.9549	163.6779		Sc II	385.7365	162.5362	
C I	815.5521		163.5892	Si IX	1047.8338		162.5294
Fe I	628.0271	163.6779		Th I	510.1866	162.5829	
Hg I	709.2313		164.5015		913.3748		161.6662
In II	492.7785	163.5845		W I	760.7865	162.5829	
N I	664.4746	161.8511		Xe IV	425.5832		161.5679

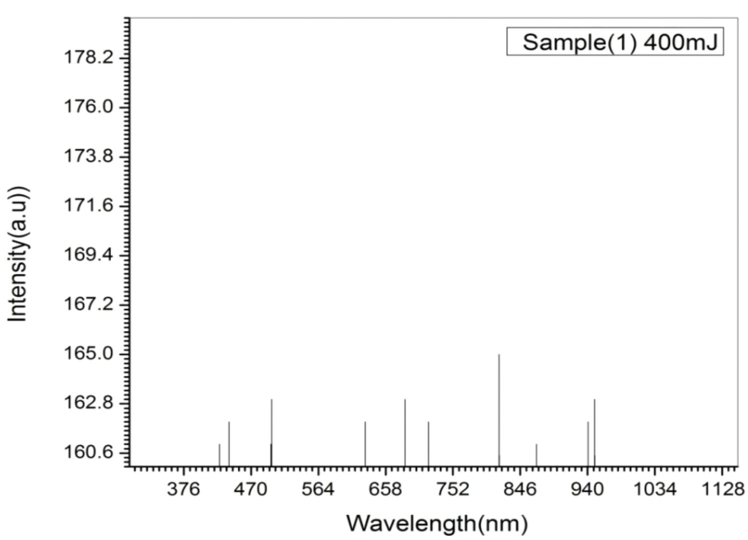

Figure 5. The emission spectra of *Adansonia* collected from Sudan using 400mJ.

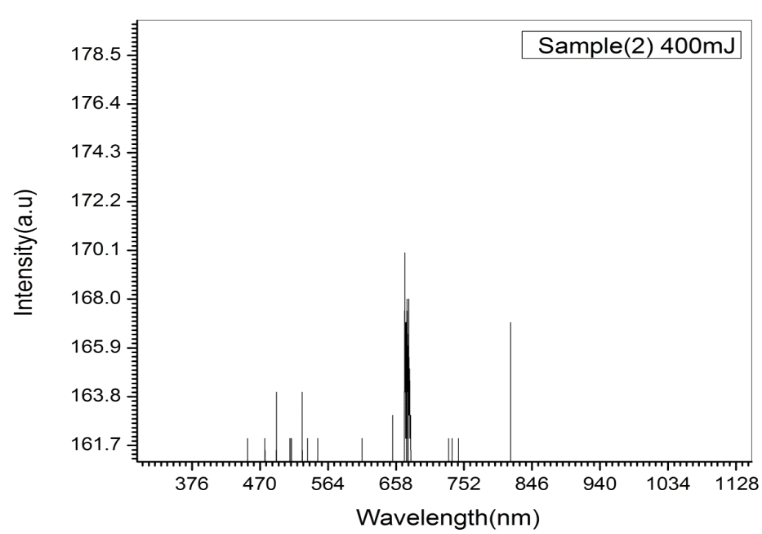

Figure 6. The emission spectra for *Adansonia* collected from Western Africa using 400mJ.

3- Irradiation with 400mJ:-

The two samples were irradiated with 400mj, resulting in the emission spectra that is shown in figure (5) and (6). The identification of the elements is displayed in table (3).

Table 3. The analyzed data for Adansonia collected from Sudan and Western Africa using 400mJ

Element	Wavelength (nm)	Intensities (a.u)		Element	Wavelength (nm)	Intensities (a.u)	
		S3	S6			S3	S6
Ag II	744.1679		162.5829	Nd II	817.2517	165.6542	
Al II	730.9487		162.5362				167.5132
Ar II	629.5379	162.6277		O I	496.7785	161.6662	
B II	652.9549		163.5430	Rb II	550.0333		162.5362
C I	671.0842		170.6116	Re I	611.4086		162.5829
	815.5521	161.1363		Sc I	493.5681		162.4479
Cr I	684.4923	163.5400		Si III	513.3970		162.5829
Eu I	669.3846		170.5701	Sr III	815.5521		162.9929
	717.5405	162.7206		Th I	476.9496		162.5829
Fe II	452.0218		162.5829		498.4781	163.8296	
	940.0111	162.6277		Ti I	536.6252		162.5362
Ho I	674.4834		167.9648	Ti III	511.8862		162.5362
In II	868.6181	161.6662		Tm II	672.7838		168.6498
Mn I	438.8025	162.5294		V I	735.8587		162.5362
MnII	950.0111	163.6821		W I	528.3159		164.6381
N II	535.1144			Xe III	491.8685		

Irradiation of *Adansonia* collected from Sudan and Western Africa (Table 1) revealed the presence of the following heavy elements: Th^{+2}, Ar^{+2} C^{+2}, Sc^{+2} and V^{+2} have been detected in both samples. Fe^{+2}, Hf,$^{+2}$ Rh^{+2}, $Cr^{+2}V^{+2}$, Hg^{+2} and In were detected in samples of Sudan only while Ti^{+2}, Al $^{+2}$and Mn were analyzed in western Africa samples. Such results were similar to the findings of Obizoba and Amaechi, (1992) and Odetokun (1996). Due to its high toxicity, Hg imposes a great menace on human health (Storelli, 2008 and Zahir *et al*. 2005), however, the effect of other heavy elements depends on the period of exposure (WHO, 2018). Most of the heavy elements are necessary for human health even if it is consumed in small amount. For instance, Cr and Fe which is present in Northern Kordofan sample and Mn is doomed to be advantageous, Fe is the main component of hemoglobin and play a great role in preserving and enforcing the immune system, having too little amount of iron might develop iron deficiency anemia (National Heart, Lung and Blood Institute, 2019), Cr plays a role in glucose metabolism and Mn which helps in calcium absorption and blood sugar regulation. Additionally, C^{+2}a, W^{+2}, Fr^{+2}, Pr^{+2}, N^{+2}, O^{+2}, Tb^{+2} and Be have just appeared in the sample collected from Sudan On the other hand, Ne^{+2}, Xe^{+2}, Ba^{+2}, Ce^{+2}, Eu^{+2}, Tm^{+2}, Ho^{+2}, Pu^{+2} and Nd^{+2} have just appeared in Western Africa sample only. These elements could be common features of the sample or the soil.

By increasing the laser energy to 200mj the identified spectra were analyzed in table (2). It is clear from the table that group of elements have been detected in the two samples such as Ar, Nd^{+2}, Rh^{+2} and Th. Moreover, Al^{+2}, B^{+2}, Fe^{+2}, In^{+2}, N^{+2}, P^{+2}, Sc and W have been observed in the fruits of west Africa only while C, Hg, Si and Xe have been observed in Northern Kordofan sample only. The presence of p in Western Africa baobab and Si in Northern Kordofan fruits which could be considered is an indicator for the soil conditions.

Boosting the laser energy to 400mj resulted in the analyzed emission spectra in table (3). Eu, Fe, Th and Xe were observed in the two samples with different emission intensities. A set of elements have been detected in Northern Kordofansamples such as Ar^{+2}, C^{+2}, Cr^{+2}, In^{+2}, Mn^{+2}, Nd^{+2} and O^{+2}. In addition to Ag^{+2}, Al^{+2}, B^{+2}, Ho^{+2}, N^{+2}, Rb^{+2}, Re^{+2}, Sc^{+2}, Si^{+2}, Sr^{+2}, Ti^{+2}, Tm^{+2}, V^{+2} and W^{+2}.

Conclusions

From the obtained results we can conclude:-

- *Adansonia digitata* fruits collected from western Sudan contains: the following elements: Al^{+2}, Ar^{+2}, B^{+2}, Be^{+}, C^{+2}, Ca^{+2}, Cr^{+2}, Eu^{+2}, Fe^{+2}, Fr^{+2}, Hf^{+2}, Hg^{+2}, In^{+2}, Mn^{+2}, N^{+2}, Nd^{+2}, O^{+2}, P^{+2}, Pr^{+2}, Rh^{+2}, Sc^{+2}, Tb^{+2}, Th^{+2}, V^{+2}, W^{+2}, Xe^{+2}. However, the analyzed data indicated that Be^{+}, W^{+2} and Nd^{+2} were found with higher concentrations as related to other elements.
- Analysis of fruits of *Adansonia digitata* collected from western Africa revealed the presence of the elements: Al, Ag, Ar, B, Ba, C, Ce, Eu, Fe, Hg, Ho, Mn, N, Nd, Ne, Pu, Rb, Re, Rh, Sc, Si, Sr, Th, Ti, Tm, V, W, Xe. C, Eu, Hoand Nd. It worth mentioning that Tm was found in high concentration compared to other elements.
- The elements in each type of *Adansonia digitata* which were obtained by LIBS can be used to differentiate between different types of the species.
- *Adansonia* of Sudan gave high concentration of Fe, Ca, Cr and Mn than Adansonia of Western Africa.
- Increasing the laser energy enhances the detection of other elements for both baobab specimens.

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