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Identification of Gum Arabic (Acacia Seyal) Constituents Using Laser Induced Breakdown Spectroscopy

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Abstract: *The aim of this work is to identify the Constituents of Gum Arabic type Acacia seyal.var.seyal. using laser induced breakdown spectroscopy (LIBS). Five Samples of the gum were collected from different locations within the gum belt of Sudan. The samples were irradiated with pulse Nd-YAG laser of pulse energy equal 80mj, The resultant emission spectra were recorded and each spectral line in the spectra were identified .It was found that the sample contain the elements C, O, H, N. Br, Ar, S, P, and the major cation Mg, Ca, K, Na, in addition to trace heavy metals Fe, Cr, Th and Ti.*

Keywords: *LIBS; emission spectroscopy; laser in Gum Arabic (Acacia Seyal)*

I. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source [1, 2]. LIBS operate by focusing the laser onto a small area at the surface of the specimen; when the laser is discharged it ablates a very small amount of material, in the range of nanograms to picograms, which generates a plasma plume. At the high temperatures during the early plasma, the ablated material dissociates (breaks down) into excited ionic and atomic species. During this time, the plasma emits a continuum of radiation which does not contain any useful information about the species present, but within a very small timeframe the plasma expands at supersonic velocities and cools. At this point the characteristic atomic emission lines of the elemental constituent of the sample can be observed. The delay between the emission of continuum radiation and characteristic radiation is in the order of 10 µs. This is why it is necessary to temporally gate the detector [3, 4]. LIBS can be used to investigate different materials especially those composed of large molecules such as Gum Arabic. *Acacia seyal* and *acacia Senegal* are two types of trees from which Gum Arabic is extracted and used as food additive. Both types of trees grow in a narrow belt of latitudes, known as the gum belt, and stretches across northern Africa to the bottom edge of Chad, including Sudan, Eritrea, Kenya, Mali, Mauritania, Niger, Nigeria and Senegal [5]. Most of the top-grade gum used in the beverage industry today comes from Sudan and Chad. Other countries, such as Uganda and Eritrea, are periodically developing acacia crops. Of the two, Acacia Senegal yields the stronger and more-expensive emulsifier. Usually the Acacia Senegal and Acacia seyal tree exude gum when they are subjected to injury of scratch of their brake intentionally or accidently. It is customary to tap these trees and allow for the gum to exude as a viscous fluid,that harden when exposed to air and became in a form of nodules that are collected later. [6.7].This work aimed to use LIBS for Identification of Gum Arabic (Acacia Seyal).

II. The Experimental part

2.1 Experimental Setup:

Figure (1) illustrates the LIBS setup which was used in this work. The LIBS system composed of Q-switched Nd- YAG Laser (Laser wavelength is 1064 nm, pulse duration 10ns, Pulse Energy 80 mj, Spot size 2-8 mm, and repetition rate 2 Hz), Ocean Optics 4000+ spectrometer, connected with PC.

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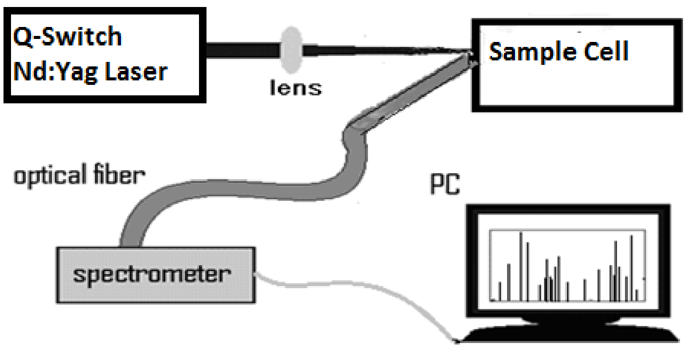

Figure (1): Schematic diagram of the setup

2.2 The Materials
Five samples of *Acacia Seyal* (Talha) obtained from different locations in Sudan. were used in this work, they are illustrated in table (1)

Table (1) Samples Grouping

Classification	**Location of samples collection**
Sample (1)	South Kordofan state
Sample (2)	North Kordofan state
Sample (3)	Blue Nile state
Sample (4)	White Nile state
Sample (5)	Gadaref Area, eastern of Sudan

2.3 Experimental Procedure:
Each sample was put in a quartz cell and irradiated by the Nd-YAG laser where the spark of the sample plasma was collected by a fiber optic to the spectrometer which was interfaces to a computer. The emission spectra were collected in the range from 200-900 nm. In order to test the homogeneity of Gum Arabic samples, several LIBS measurements were performed at its surface. The recorded spectra of the samples were analyzed using NIST data.

III. Results and discussion

Figures (2) to (6) show the LIBS emission spectra for the samples of *Acacia Seyal* (Talha), after irradiation with 80 mJ pulse energy. Atomic spectra database and Hand book of Basic Atomic Spectroscopic Data were used for the analysis of the emission spectra .Each spectral line was assigned to the corresponding constituent element or ion in the sample, Table (2) lists the wavelength and intensities of the different spectral lines in the emission spectra for the samples studies along with the constituent elements corresponding to each line.

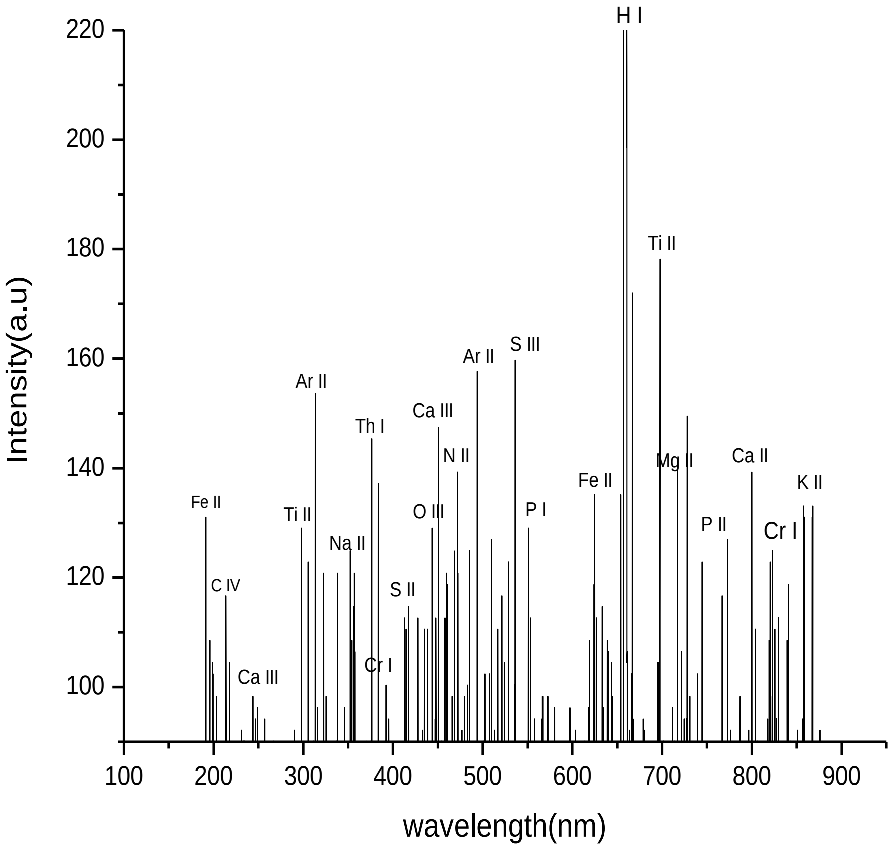

Figure (2): LIBS emission spectrum of sample (1)

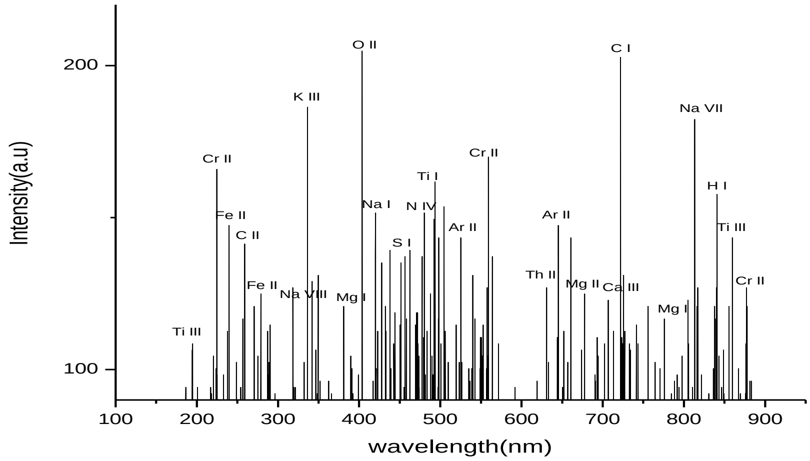

Figure (3): LIBS emission spectrum of sample (2)

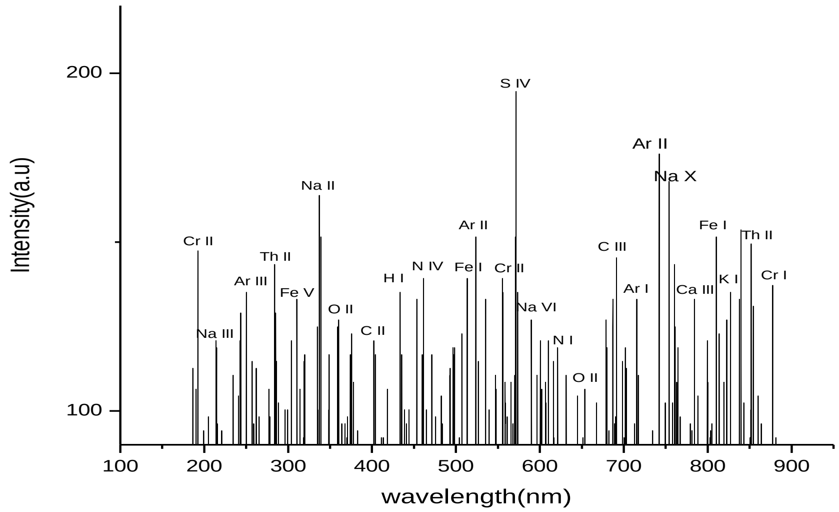

Figure (4): LIBS emission spectrum of sample (3)

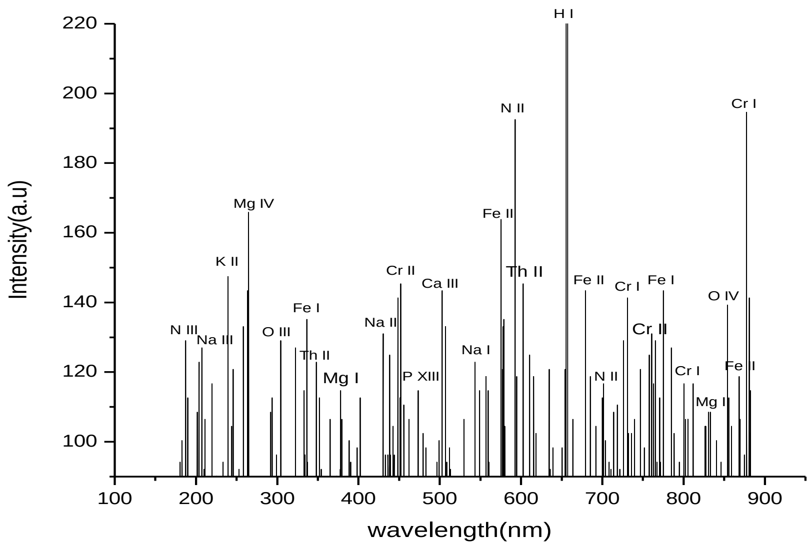

Figure (5): LIBS emission spectrum of sample (4)

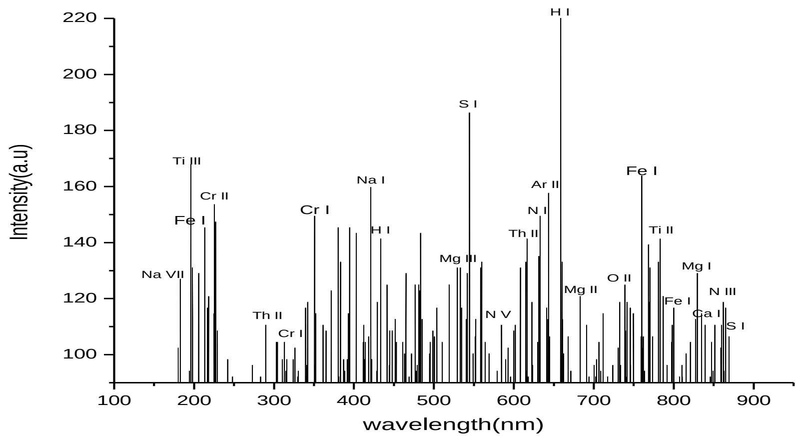

Figure (6): LIBS emission spectrum of sample (5)

Table (2): The analyzed data of the samples after irradiation by laser energy of 80 mJ

Element	λ(nm)	Intensity of emission (a.u)				
		(s1)	(s2)	(s3)	(s4)	(s5)
Fe I	217.0590		97.3129		120.3167	123.9377
	224.2336	99.8689	168.0284			156.8814
	314.4824		96.8869	108.2768		101.8569
	345.0688		109.3828	124.3637		
	401.3327	146.8705		142.8235	115.9148	146.8705
	516.5037	113.8558	118.1157	142.3975	126.3517	135.4396
Fe II	185.7174	103.8448	97.7389	116.3407		
	205.7307		97.3129	124.3637	126.3517	132.0316
	221.5904	95.8219	168.0284	97.8099		
	258.5961		144.8115	118.6837	136.7886	
	510.0844	126.3517	105.2648	126.3517	102.2829	106.9688
	633.5628	118.3287	105.6908		123.9377	151.9115
	746.8458	116.3407		179.8143	124.3637	119.9617
Fe III	364.3269			98.5909	109.5248	112.2938
	436.4504	99.8689		103.8448	103.8448	
	512.7276		105.2648	142.3975	102.2829	94.5439
	775.5442	114.2818	119.8907		146.4445	109.3828
Na I	249.1559		104.8388		123.9377	95.8219
	261.2394	96.5319	144.8115	115.9148		
	289.5601	108.2468		106.5428	111.4418	113.8558
	419.8356	112.2938	153.9705	109.9508		109.9508
	432.6743	114.2818	124.1507		134.3746	162.9164
	589.4944		97.7389	130.3276		100.1529
	691.7147	114.2818	113.9268	148.8585	108.1758	124.1507
Na II	242.7364	155.6744		132.3156		101.4309
	254.8200	97.8099	119.9617		95.8219	
	274.0781		107.4658	136.7886		99.8689
	316.3705	122.3757	130.0436	108.2768		101.8569
	519.1470	103.8448	118.1157	130.7536	102.2829	127.5587
Na III	203.0875			101.8569	126.3517	
	211.3949			124.3637	109.9508	148.4325
	323.9227	122.3757	96.8869		130.3276	101.4309
	713.6161	128.4107	116.1987	97.8099	112.2938	
Ca I	272.1901		124.1507	108.2768		99.8689
	428.8982	114.2818	137.9956		134.3746	121.9497
	616.9480	103.4188		114.9027	121.9497	144.3955
	720.0355	107.8918	193.1622		95.8219	
	734.7623	101.8569	112.0098	97.8099	105.9038	127.8427
Ca II	420.5908	112.2938	153.9705			162.9164
	423.2341	112.7198	115.3468			
	608.6406			111.8678	127.9847	134.3036
	757.0413	150.4915	124.1507	146.4445	127.9847	
	849.1781	132.7416	109.3828	152.8345	101.3409	107.8918

Ca III	199.3114	134.8006	127.5587	146.8705		146.0185
	535.0066			136.7886		133.9486
	800.0888	122.3757		123.9377	119.8907	
	823.5006	103.8448		130.2566		
Mg I	265.7707	112.2938		98.5909	168.9513	112.2938
	382.0746			112.2938		136.3626
	548.6006	95.8219		113.4298	117.9027	103.4189
	631.6748	150.9175		114.2818	124.3637	118.1157
	751.3771		124.1507	170.0873	101.3409	113.5008
	781.2083	114.2818		99.8689		144.3855
	805.3753	130.7536	126.3517		109.5958	
	847.2900	132.7416			97.8099	107.8918
	860.8840	138.8476	105.6908	108.2468		
Mg II	359.7956	98.2359	98.8749	130.7536		114.2818
	427.0102		137.9956		134.3746	121.9497
	545.2021	103.8448		113.4298	125.9257	188.1922
	787.6277	132.7416		108.2468		123.7247
	811.4171	112.2938	184.7132	154.8225	119.8907	
Mg III	183.0741	108.2468	116.1987	136.7886	103.8448	130.6826
	450.0444	150.1365	137.9956	108.2468	148.4325	116.3407
	491.5815	161.2834	164.7624			146.0185
	562.5721		140.6936	111.8678		
	692.4700		113.9268	148.8585	108.1758	113.5008
	704.5535	94.5439	126.3517	140.4096	119.9807	101.9989
K I	297.1123	132.3156	95.4669	103.8448	99.8689	
	327.6988	156.8814		136.7886		105.4778
	690.9595		113.9268	148.8585	97.8099	113.5008
	710.9729	119.6067		101.4309	112.2938	117.3347
	785.7396		95.4669	136.3626	130.3276	
	850.3109	136.7886	103.3478	152.8345	121.9497	113.5008
K II	203.4651	101.8569		101.8569	126.3517	
	368.8582	140.4096	123.7247	112.2938	117.9027	148.4325
	498.0008		146.7285		102.7799	111.8678
	579.1870	99.4429			138.4216	97.7389
	681.5193	114.2818	126.3517	154.8225	109.5958	99.2299
K III	334.1181		187.5532	137.3894	138.4216	152.8345
	388.4940	140.4096	107.1818		103.8448	102.2829
	457.5966	123.9377	139.8416	136.7886	113.4298	
	576.5437	175.3413	103.3478	101.4309	166.9634	97.7389
S I	467.7920	126.7067		102.5669		132.3156
	549.7334	132.3156	134.3036	103.8448	125.9257	103.4189
	558.0408		172.9983	111.0158		
	572.3900	101.8569		197.8481	166.9634	
	595.8018		97.7389	113.8558		105.2648
	724.1892	109.5248	134.3036			99.6559
	792.9142		97.7389	108.2468		99.6559
	816.3260	128.4107	130.0436	126.3517	121.9497	119.9617
S II	361.6836	123.9377	98.8749	130.7536	109.5248	114.2818
	500.6441	105.9038	141.9716	124.3637	146.0185	146.8705
	522.9231	119.8907		154.1125		
	536.8947	162.9164	103.7738	136.7886	146.4445	133.9486
	698.1341	181.3762		117.0507		99.6559
	740.4264	105.4778	112.0098	179.8143	108.6728	122.2337
S III	252.1768		104.8388		95.8219	
	337.5166	123.9377		137.3894	125.9257	119.8907
	632.4300	117.9027	105.6908	114.2818	123.9377	151.9115
	702.6654		112.0098	122.3757	119.9807	101.9989
C I	292.5810	95.8219			111.4418	
	473.4562	114.2818	121.8077	101.8569	117.5477	103.8448
	529.3425	125.6417	156.4554	117.0507	109.1698	134.3746
	568.9915	99.8689	140.6936	197.8481	138.4216	103.7738
	601.4660	109.5248	134.3036		149.2845	111.9388
	763.4606		105.6908	121.9497	132.3156	
C II	511.9724	123.9377	98.8749	130.7536	102.2829	114.2818
	625.2554	138.2416		121.0977		121.3817
	677.7432	97.8099	127.8427	130.7536	146.4445	
	803.1097	114.2818	126.3517		109.5958	99.2299
C III	218.1919		107.8918		120.3167	123.9377
	524.4335	108.2468	146.3025	117.0507		
	794.8023		97.7389	123.9377	97.0999	99.6559

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	851.8214	95.8219	123.7247	152.8345	142.8235	113.5008
N I	336.0062	123.9377	187.5532	137.3894	138.4216	
	493.4695	161.2834	164.7624	116.3407		107.8208
	639.2270	111.8678			101.4309	97.7389
	765.3487	119.6067	105.6908	121.9497	132.3156	
	789.8933	101.8569	99.2299		105.4778	123.7247
	856.7303	136.7886	123.7247	134.8006	107.8208	
N II	384.7179	103.8448				136.3626
	462.1279	123.9377	141.9716	142.8235	109.5248	108.2468
	531.9857	125.6417	156.4554	95.8219	146.0185	133.9486
	593.1585	95.8219	97.7389	130.7536	195.0081	105.2648
	860.1288	136.7886	146.3025	122.3757	119.9807	121.8077
N III	210.6397			116.3407	109.9508	148.4325
	471.1905	142.3975	121.8077	120.3167	117.5477	103.8448
	644.5135	111.8678	151.2105	121.0977		160.644
O I	201.1994		96.8869		126.3517	
	510.8396	130.7536	105.2648	142.3975	121.9497	144.3955
	646.4015		151.2105	107.8918		
	777.4322	95.3959	119.8907		146.4445	
	840.8707	121.9497	161.0704	105.4778	103.8448	113.9268
O II	296.469	132.3156	95.4669	103.8448	115.9148	
	302.398	126.3517	101.1469	123.9377	132.3156	148.8586
	444.7578		122.2337	103.8448		112.2938
	460.2398	123.9377	141.9716	142.8235	109.5248	108.2468
	762.7054	142.3975	105.6908	123.9377	134.3746	127.8427
O III	319.3913	126.3517	130.0436	123.9377	132.3156	148.8586
	610.5286	175.3413	99.6559	123.9377	127.9847	134.3036
	729.4757	152.8345	112.0098		144.8825	
	795.9351	95.8219	97.7389	154.8225	97.0999	99.2299
	812.1723	128.4107	184.7132		119.8907	
Cr I	194.0248	112.2938	112.0098	150.9175		171.3653
	212.1501			124.3637		148.4325
	234.4291	95.8219	101.`1469	114.6368	97.8099	
	456.3637	150.1365	156.4554	95.8219	146.0185	
Cr II	245.7574	101.8569		132.3156	123.9377	101.4309
	253.6872		119.9617		95.8219	
	275.9662	140.4096	107.4658	109.9508		99.8689
	539.5379	162.9164	134.3036a	103.8448		
	554.2647	132.3156		142.3975	121.9497	115.9148
	572.7676	101.8569	134.3036	197.8481	166.9634	103.7738
Cr V	637.7165	117.9027	105.6908		101.4309	151.9115
	731.3638		112.0098	97.8099	144.8825	121.8077
	798.9560	142.3975	107.8918	123.9377	119.8907	119.5357
Ti I	259.3513	97.8099	144.8115	118.6837	136.7886	
	370.7463			98.5909		126.3517
	478.3651	95.8219	154.9645		117.5477	127.9847
	562.1945	101.8569	140.6936	111.8678	138.4216	136.3626
Ti II	229.1426	95.3959	127.5587	146.8705		95.8219
	430.7863	95.8219	105.2648		134.3746	
	521.0350	119.8907	193.1622	154.1125	95.8219	127.5587
Ti III	350.7330	128.4107	133.8776		115.9148	152.8345
	451.9324	142.3975	137.9956	136.7886	148.4325	116.3407
	755.1532		124.1507	170.0873	127.9847	
	829.9200	115.7018	94.4669		112.2938	131.9606
Br I	238.582	101.8569	150.4205		150.9175	
	422.478		115.3468			162.9164
	518.769	108.2468	118.1157	142.3975		127.5587
	668.302	175.3413		105.9038	109.5248	109.0988
	813.305		184.7132	126.3517	119.8907	103.3478
Br II	417.9475	117.4057	99.2299			
Ar I	375.2776	148.4325		126.3517		
	437.9609	114.2818		103.8448	127.9847	
	556.1528	97.0999	146.3025	142.3975	121.9497	134.3746
	565.2154		140.6936	111.8678		107.4658
	654.7090	138.4216	105.6908	108.6728		
Ar II	453.8205	150.1365	139.8416	136.7886	113.4298	148.4325
	538.4051			103.8448		
	783.8516	115.7018	95.4669	136.3626	130.3276	144.3855
Ar IV	244.6246	101.8569		132.3156		101.4309
	464.7712	126.7067	141.9716	102.5669	109.5248	132.3156

	717. 3922	144.4565	126.3517	136.7176	113.0038	95.4669
Th I	383.9626	140.4096	123.7247	126.3517		136.3626
	419.4580		153.9705	109.9508		109.9508
	764.2159	119.6067	105.6908	121.9497	132.3156	
	778.5650	95.3959		99.8689	105.4778	
	792.5366		97.7389		97.0999	99.6559
Th II	376.7880	148.4325			117.9027	
	478.3651		154.9645	126.3517		127.9847
	537.2723	162.9164		136.7886		
	594.6690	111.8678	130.4696	121.0977		105.2648
	858.6183	136.7886	146.3025		107.8208	121.3817
P I	274.8334		107.4658			99.8689
	342.4255		131.9607			121.8077
	551.6215	132.3156	117.6897	142.3975	149.2845	115.9148
H I	366.2150	103.8448	95.4669	126.3517		
	393.0253	115.0628				148.8586
	410.395	114.7078		96.2479		114.7078
	434.184	127.9847	142.6815	138.8476	134.3746	145.3085
	486.0502	222.6269	127.8427		127.9847	146.0185
	656.5970	103.8448	105.6908		223.0529	222.1179
	825.3887	113.0038		130.2566	108.2468	115.7728
	832.5633				111.8678	

The elements constituting the samples observed in the emission spectra were C, H, N, O, S, P, Fe, Na, Ca, Mg, K, Cr, Br, Ti, Ar, and Th.These elements reflects the established composition of Gum Talha reported in scientific literature [8]. Gum Talha is a natural polysaccharide builds mainly from galactose, arabinose, rhaminose and glucuronic acid, with small proportion of proteineceous material [9]. Hence it is expected to observe elements like C, H, O, as main constituent of carbohydrates. Also the presence of the elements like; N, S and P is expected as Gum Talha contains proteineceous material. The elements Mg, Ca, K and Na were observed by LIBS analysis in all samples collected from the different locations. This observation is in agreement with previous studies, [10.11]. Also the elemental analysis of gum Talha by LIBS provide a supportive evidence for the presence of heavy metals like Fe and Cr which had been reported by other researches.[12]. It is interesting to report, for the first time, the presence of Br, Ar, Ti and Th in Gum Talha. These elements have not been observed by techniques usually used for elemental analysis of gum, such as Atomic Absorption spectroscopy (AAS) and inductively coupled plasma spectroscopy (ICP). It is also of interest to note the presence of higher ionization states of some of the elements present in the gum samples subjected to study such as: Fe^{+3}, Fe^{+2}, Cr^{+3}, Th^{+2}, Ca^{+2}, Cr^{+5},Ti^{+2} and Ti^{+3}.The results obtained in this work demonstrated that LIBS is a suitable technique for elemental analysis of gum Arabic and it is also a sensitive analytical method capable of detecting elemental species that could not be observed in other techniques.Although the study had demonstrated that Gum Talha consist of uniform elemental composition, the influence of location of sample collection was well presented and evident from the differences in the emission intensities of the same elements in the samples.

IV. Conclusions

Elemental analysis of gum Talha can be done conveniently and with great accuracy by LIBS technique. Gum Talha was found to contain elements like Ar, Ti, Br, and Th, which had been reported here for the first time.

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