1

Identification of Elements in Some Sudanese Gasoline Types Using Nd:YAG Laser Induced Breakdown Spectroscopy

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) employs a low-energy pulsed laser (typically tens to hundreds of mJ per pulse) focused on sample to generate plasma that vaporizes a small amount of the sample. A portion of the plasma emission light is collected and a spectrometer disperses the light, emitted by excited atomic and ionic species in the plasma, a detector records the emission signals, and electronics take over to digitize and display the spectra [1].

LIBS is a type of atomic emission spectroscopy (AES). It has become a powerful analysis technique for both laboratory and field use. The main purpose of LIBS, like AES, is to determine the elemental composition of a sample (solid, liquid, or gas). The analysis can range from a simple identification of the atomic constituents of the sample to a more detailed determination of relative concentrations or absolute masses [2].

Examination of the emitted light provides the analysis because each element has a unique emission spectrum useful to "fingerprint" the species. Extensive compilations of emission lines exist [3 - 5]. The position of the emission lines identifies the elements and, when properly calibrated, the intensity of the lines permits quantification.

Q-switched lasers had the capability of producing high focused power densities from a single pulse of short duration sufficient to initiate breakdown and to produce analytically useful laser plasma.

Typically, however, the signals from many laser plasmas are added or averaged to increase accuracy and precision and to average out non-uniformities in sample composition. Depending on the application, time-resolution of the plasma may improve the signal-to-noise ratio or discriminate against interference from continuum, line or molecular band spectra [6].

Today LIBS is used to analyze gases, liquids, particles entrained in gases or liquids, and particles or coatings on solids. Liquids can be analyzed by forming the laser plasma on the liquid surface or on drops of the liquid [7, 8]. If the liquid is transparent at the laser wavelength, plasma can be formed in the bulk liquid below the surface [9].

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LIBS has the following advantages compared with some non-AES - based methods of elemental analysis [10]:

- Provide qualitative and quantitative information about the sample composition.
- Simultaneous multi-element detection capability.
- Simplicity.
- Provide real-time analysis.
- No need for sample preparation.
- Allows in situ analysis requiring only optical access to the sample.
- Adaptable to a variety of different measurement scenarios.

This work aimed to identify the elements in three different types of Sudanese gasoline. The bulk of a typical gasoline consists of hydrocarbons with between 4 and 12 carbon atoms per molecule (commonly referred to as C_4-C_{12}). Some of gasoline types contain small amounts of other elements, including sulfur, nitrogen, oxygen, and some trace metals. The identification of such elements is important in determination of gasoline quality due to their effects on combustion process.

The identification here is based on the use of laser induced breakdown spectroscopy (LIBS) technique, in which high peak power Q-switched Nd-YAG laser focused on the sample, to produce plasma emission of discrete lines.

These lines are the fingerprints of the atoms and ions constitute the sample where the line intensity is proportional to element amount in the sample. By recording these emission lines one can get qualitative information and identify the elements in each sample.

2. Materials and methods

A schematic diagram of the experimental setup used in this work is shown in figure (1).

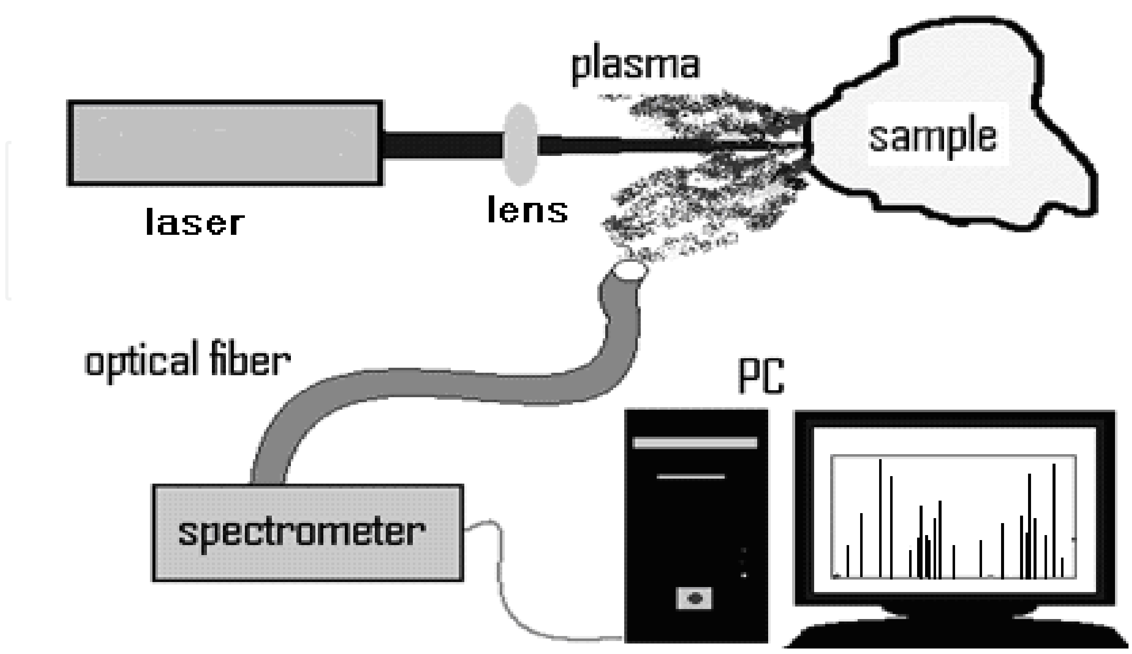

Fig. 1. Schematic diagram of the setup

The experimental setup consists of:-

i. Q-switched Nd: YAG laser supplied from XSD Hua Zhong Precision Instrument Factory, model LRH786T with 10 ns pulse duration and 0.5 Hz repetition rate. The pulse energy of this laser is adjustable starting from 12.57 up to 23.8 mJ.

ii. Spectrometer model USB 4000-UV/VIS, supplied from ocean optics - USA, attached with optical fiber and interfaced to computer with Windows operating system. The modular USB4000 is responsive from (170 -900) nm. The detector is Toshiba TCD1304AP linear CCD array detector, 3648 pixels, with a spectral response in the range (150 -950) nm.

iii. The software "SpectraSuite", supplied from Ocean Optics, was used in this work to control the Ocean Optics USB spectrometer.

iv. Samples: Three different types of Sudanese gasoline, collected from three different refineries, were investigated here. These are petroleum-derived liquid mixtures primarily used as a fuel in internal combustion engines. It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating. Small quantities of various additives are common, for purposes such as tuning engine performance or reducing harmful exhaust emissions.

The experimental procedure was done as follows:

- Laser energy was adjusted to obtain sufficient peak power needed to form plasma.
- A laser pulse was fired on the sample cell without the sample and the plasma emission spectrum was recorded and saved as background.
- After that the plasma emission spectrum of every sample was recorded.
- The plasma spectrum was processed by subtracting the background.
- By referring to the atomic spectra database, the atoms and ions in the samples were identified.

3. Results and discussion

Figures (2), (3) and (4) show the emission spectra, in the range from 179 nm to 859 nm, of the three gasoline samples (1, 2 and 3), respectively. The laser energy per pulse was 23.4 mJ and the pulse duration was 10 ns that lead to peak power equals 2.34 $X10^6$ W. The power density was $1.32*10^8$ W/cm^2.

Atomic spectra database was used for the spectral analysis of the tested samples and the results are listed in table (1).

The three spectra of the samples show the essential atoms of the hydrocarbons that form the gasoline (C and H) with different amounts for each sample. There were also common relatively small amounts of other elements, including (Ar, Co, Fe, N, Ni, O, W, Si and Sc), found in all the three samples with different amounts. The Argon, Cobalt, Iron and Nickel were very low in sample 1 while larger amounts of them were found in samples 2 and 3. Silicon and Scandium were found nearly equal in all the three samples. The presence of all mentioned elements is due to the origin of the crude oil. The Oxygen atoms were found with relatively smaller amount in sample 1 compared with sample 2 and 3, it seemed that it was added in the refinery to reduce carbon monoxide and unburned fuel in the exhaust gas thus reducing smoke.

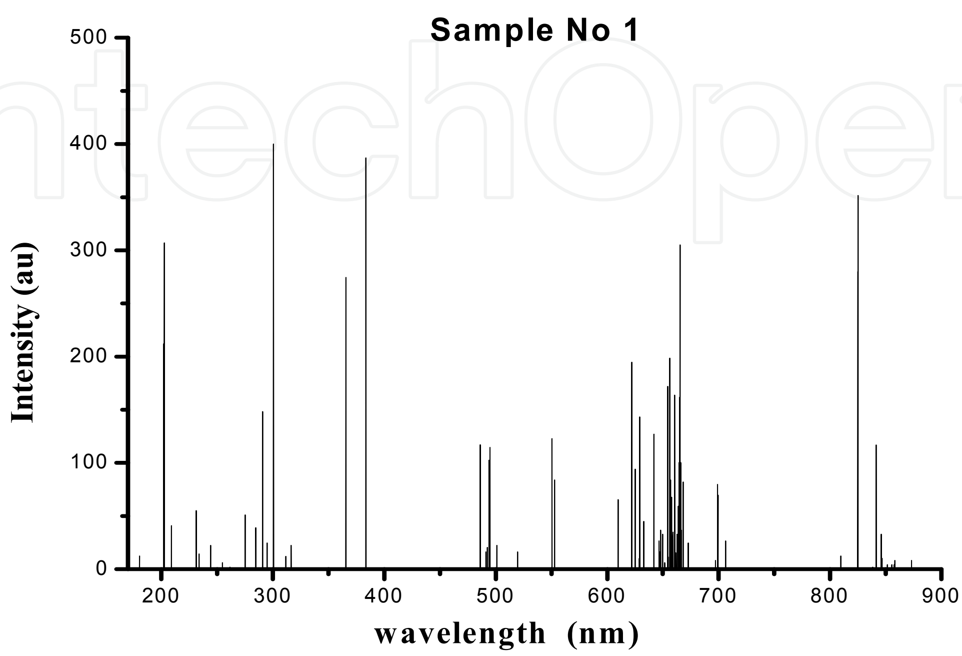

Fig. 2. LIBS emission spectrum of sample No 1

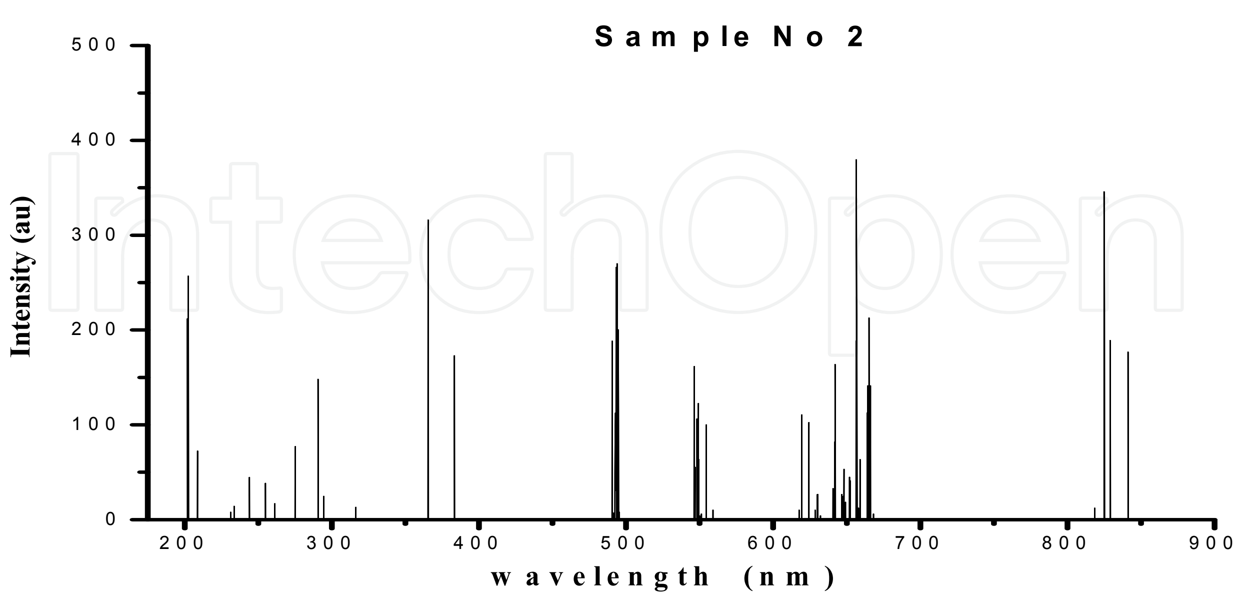

Fig. 3. LIBS emission spectrum of sample No 2

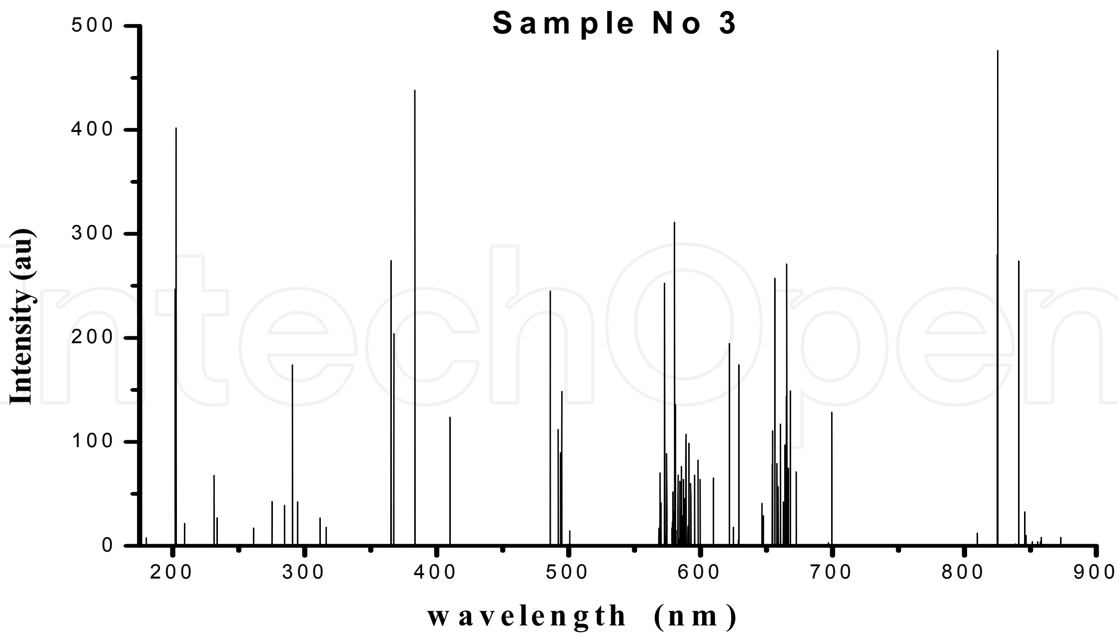

Fig. 4. LIBS emission spectrum of sample No 3

The appearance of Tungsten in the spectra was due to tiny fraction of the background lamp intensity that was not stored due to the change in its intensity.

The ratio of hydrogen to carbon determines the octane rating which is the measure of resistance of petroleum to engine knocking that damage it quite quickly. The octane rating decreases with carbon chain length and increases with carbon chain branching [11]. High rating means more hydrogen atoms with the same carbon atoms. That depicts that sample 1 has lower ratio (2.76) and lower rating, while samples 2 and 3 have higher ratios, 3.76 and 2.84, respectively.

Line Wavelength λ (nm)	Sample no. (1)		Sample no. (2)		Sample no. (3)	
	Element	Intensity (a.u.)	Element	Intensity (a.u)	Element	Intensity (a.u)
180.29	Rb II	12.29			Rb II	7.9
202.03	C II	212	C II	212	C II	247
202.64	O I	307.1	O I	256.9	O I	402.04
208.95	C III	40.96	C III	72.4	C III	24.5
231.43	O III	55	O III	8.19	O III	68.01
233.74	Na II	18.37	Na II	13.34	Na II	27.34
244.04	Fe II	22.53	Fe II	44.7		
254.94	O III	6.14	O III	38.4		
261.43	C III	2.05	C III	17	C III	42.76
275.18	C III	51.2	C III	77.24	C III	1721
290.88	C II	148.4	C II	148.4	C II	174.09
294.8	C III	24.58			C III	42.31
311.61	Hg II	12			Hg II	27.04
316.37	Na II	22.53	Na II	13.2	Na II	18
365.66	H I	274.5	H I	316.2	H I	387.1

Line Wavelength λ (nm)	Sample no. (1)		Sample no. (2)		Sample no. (3)	
	Element	Intensity (a.u.)	Element	Intensity (a.u)	Element	Intensity (a.u)
367.62					H I	204.1
383.54	H I	387.1	H I	173	H I	387.1
410.17					H I	123.84
486.13	H I	117			H I	245.13
491.74			B III	7.37		
492.34	O II	20.48	O II	49.15	O II	112.06
492.73			Fe I	112.64		
492.93			Na VI	36.86		
493.33			C I	266.24		
493.53			N I	83.97		
493.92			Fe I	270.33		
494.12	O IV	102.4			O V	89.51
494.32			K II	11.44		
494.71	O I	2.05	O I	200.7	O I	36
494.91	O II	114.69	O II	116.73	O II	148.72
500.85	O III	22.53			O III	14.52
545.22			W I	204.8		
546.39			Mg II	161.79		
546.97			W I	55.3		
548.33			Co I	106.49		
549.11			Kr I	122.88		
549.50			Ni I	63.49		
551.25			Ti I	6.14		
554.56			Xe III	100.35		
559.03	Ca I	3.97	Ca I	10.24		
568.33					V I	8.86
568.52					Th I	17.06
569.49					Ni I	70.3
569.88					Hg II	15.01
570.07					Ar I	41.63
572.97					S II	10.91
574.32					Fe I	88.73
575.29					Kr II	13.92
578.38					O II	17.06
579.15					Fe I	51.87
579.73					S II	33.44
580.5					C I	311.26
581.46					Xe I	15.01
581.65					Ne I	19.1
582.81					Fe I	25.25

Line Wavelength λ (nm)	Sample no. (1)		Sample no. (2)		Sample no. (3)	
	Element	Intensity (a.u.)	Element	Intensity (a.u)	Element	Intensity (a.u)
583					Xe I	68.25
583.19					K I	6.82
583.58					W I	6.82
585.12					Fe I	25.25
586.27					W I	29.34
587.43					He I	19.13
587.81					Co I	45.73
588.96					C I	84.64
589.16					C II	107.17
590.31					O II	6.82
590.69					Fe I	19.1
591.27					S II	92.15
592.81					N II	47.77
595.49					Kr I	68.25
598.37					Fe I	82.59
598.94					W I	0.67
599.9					N I	64.16
609.83	C II	65.53			C II	65.53
624.29			V I	102.4		
625.01	Ne II	94.21				
625.05					Ne II	18.1
628.84	Sc I	10.24	Sc I	10.24	Sc I	5.84
629.22	C I	143.36			C I	174.06
629.98			Rb I	26.62		
630.36			Kr II	26.62		
632.06			La II	4.1		
632.82	Ne I	45.06				
640.56			N I	32.77		
641.13			Eu I	26.62		
641.88	S III	126.97	S III	81.92	S III	79.4
642.26			N I	163.8		
646.59	O V	26.62			O V	41
646.78			Ni II	26.62		
647.34			Sc II	12.29		
647.53	Na II	16.38			Na II	29.22
647.72			Fe I	24.58		
648.1	Ar I	36.86	Ar I	53.25		
649.22			O II	18.43		
649.79	Nb I	32.77				
651.67	Ne II	6.14				

Line Wavelength λ (nm)	Sample no. (1)		Sample no. (2)		Sample no. (3)	
	Element	Intensity (a.u.)	Element	Intensity (a.u)	Element	Intensity (a.u)
651.85			Si I	45.06		
652.42			Si III	40.96		
654.37	O V	172.03				
654.67	Li II	11.59			Li II	78.56
655.61					Al III	6.82
656.29	H I	198.65	H I	379.8	H I	257.2
657.8	C I	67.58			C I	79.18
658.76	C I	26.62			C I	49.02
658.98	Si I	34.82			Si I	57.13
659.17			C IV	63.49		
660.57	C I	163.84			C I	117
661.41	Fe III	15.55				
662.73	O II	32.77			O II	42.54
663.84	Co I	15.86			Co I	97.1
664.03	S II	59.39	S II	112.64	S II	97.06
664.40	O IV	100.35	O IV	141.31	O IV	67.41
664.97	N I	161.79			N I	143.16
665.25			O II	212.99		
665.46	C I	305.15			C I	271.08
665.53	Mg IV	86.01			Mg IV	32.61
666.66	O II	100.35			O II	74.85
666.69	N I	36.86				
668.22	O V	81.92			O V	149.22
668.33			Th I	6.14		
672.61	N I	24.58			N I	71.21
697.08	Kr II	8.19			Kr II	3.02
699.10	W I	79.87				
699.47	S I	69.63			S I	128.6
706.28	Ni I	26.62			Ni I	43.01
824.99	H I	351.7	H I	346	H I	476.34
829.23			H I	189.16		
838.37					Cl II	2.05
841.33	H I	116.8	H I	177.03	H I	274.29
845.92	Ne II	32.77			Ne II	32.77
846.61	Fe I	10.24				
851.57	S II	4.1				
855.50	Hg I	4.1				
857.54	C II	4.1				
858.22	Fe I	8.19				

Table 1. Analysis of emission spectra for the three gasoline samples

Also there were relatively small amounts of neutral atoms which were not common for the three samples including (Ca, Eu, He, Hg, K, Kr, Nb, Ne, S, Th, Ti, V, Xe). This depicts that the original crude oils were brought from various fields and different refinery techniques were used to get the three types of gasoline, it is also may be due to additives added in order to enhance the gasoline quality.

Beside neutral atoms, ions of different amounts and ionization stages were found in the three samples like: Al III, B III, C II, C III, Fe II, Fe III, Hg II, K II, Kr II, Li II, Mg II, Mg IV, N II, Na II, Ni II, O II, O III, O V, S II, S III and Si III. Some of these ions were produced via the ionization of neutral atoms by the laser power density itself.

4. Conclusions

From the experimental results obtained in this work one can conclude that

- LIBS technique showed that the essential atoms forming the samples (Hydrogen and Carbon) appeared with higher amounts compared with other elements (like Calcium, Helium, Mercury, Potassium, Krypton, Neon, Niobium, Scandium, Silicon, Thorium, Titanium, Vandite) that were exist with very lower amounts.
- LIBS has the ability to detect, sensitively, almost all the elements and ions in gasoline samples.
- LIBS is a very good diagnostic technique that can be used in investigation of elements in liquid samples and to get the octane rating, in liquid fuels, precisely.

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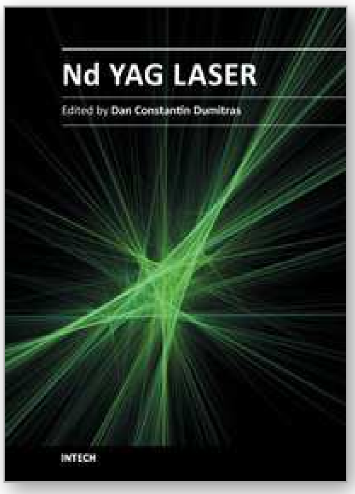

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Discovered almost fifty years ago at Bell Labs (1964), the Nd:YAG laser has undergone an enormous evolution in the years, being now widely used in both basic research and technological applications. Nd:YAG Laser covers a wide range of topics, from new systems (diode pumping, short pulse generation) and components (a new semiorganic nonlinear crystal) to applications in material processing (coating, welding, polishing, drilling, processing of metallic thin films), medicine (treatment, drug administration) and other various fields (semiconductor nanotechnology, plasma spectroscopy, laser induced breakdown spectroscopy).