

Spectroscopic Study of Plastic Water Bottles and Bottles Caps Using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract:

This study was conducted to analyze the components of the plastic materials used in water bottles and in the caps of water bottles using laser induced breakdown spectroscopy (LIBS). Bottles samples were collected from some factories in Sudan.

The samples were collected pre- and post-used. Multiple emission spectra were obtained from 3 different manufacturers for 3 different bottles were irradiated by Nd: YAG laser at 266 nm with pulse energy 80mJ. Atomic Spectra Database was used for the spectral analysis of the plasma emitted from those samples. The results showed all elements present in plastic water bottles and bottles caps, that are Mn II, Ca II, Cl II, S II, N II, K II, Mg I, Pm II, O II, Mo I, Mg II and F. All these elements are normal and this are useful for recycling only one times.

Keywords: *Laser-induced breakdown spectroscopy (LIBS), Plastic materials, Plasma, Polymers, Waste recycling.*

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I. Introduction:

The growing and continuous use of plastic products is one of the reasons in many countries for the generation of large amounts of residue[1]. Currently, the worldwide consumption per year is over 380 million metric tonnes[2]. Around 50 percent of the use is for disposable products such as packaging materials, water bottles, medical equipment and disposable consumer items, etc[3,4]. A great number of packaging materials are made from polymers, such as bottles and boxes. For the manufacture of packaging materials, additives such as plasticizers, antioxidants, antistatic agents and lubricants may be used. The worst consequence of plastic production is the environmental degradation[5]. Recycling is a solution to this problem and the first step is the identification and classification of the polymers and determination of different elements present in it[6]. So we need proper instrumentation to analyse plastics. LIBS provides a unique advantage and fast, rapid technique for plastic materials characterization.

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy (AES) method which uses a laser-generated plasma as a source for hot vaporization, atomization, and excitation. The plasma is produced by intense optical radiation [7,8]. A LIBS measurement is carried out by forming a laser plasma on the sample and then collecting and spectrally analyzing the plasma light. Qualitative and quantitative analyses are carried out by monitoring emission line positions and intensities[9]. LIBS has evolved as a versatile elemental analysis method that attracted tremendous attention due to some of its features including rapid elemental analysis, no prior sample preparation, simultaneous detection of a number of elements (high and low Z), low detection limits (micro / nano gram levels), detection capability of micron size area / thickness, and in situ / remote analysis possibility[10,11]. This research analyzes plastic water bottles and bottle caps using LIBS technique led to the determination of different elements present in it.

II. Materials and Methods

Samples Preparation:

The samples used in this research, were plastic materials used as drinking water containers in Sudan, were collected from manufacturing factories located at Khartoum city, Sudan. The samples were collected before and after used, this plastic bottles samples were sterilized and washed with distilled water before analyze by LIBS device to avoid any type of contamination. Also the samples were cut for slices it is size 3×3 cm², and thickness 2mm. The total number of samples of water bottles and water bottle caps is 9 samples. Details are shown in table (1) which illustrates water bottles and water bottle caps.

Table (1) Water bottles and Water bottle caps

Bottle Before use	Bottle After used	Bottle cap
Sample (M11)	Sample (M21)	Sample (M31)
Sample (M12)	Sample (M22)	Sample (M32)
Sample (M13)	Sample (M23)	Sample (M33)

The Experimental Setup:

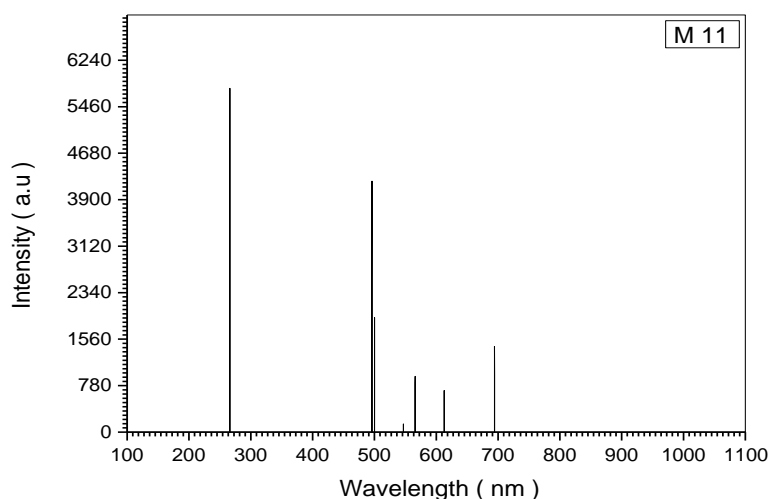
Laboratory preparations used in this research is a RT100-B system (Applied Spectra, Inc). The RT100-B uses Laser Induced Breakdown Spectroscopy (LIBS) to identify unknown elements in a given sample. The RT100-B consisted of a neodymium-doped yttrium aluminum garnet (Nd:YAG) Laser with a wavelength of 266 nm has pulse energy 80 mJ . Where a laser was used to separate part of the target material and generate the plasma. The light from the plasma is collected via collection optics; subsequent spectral analysis of the light collected on the optical fiber yields the composition of the sample. The plasma spectrum consists of narrow spectral lines emitted from atoms and ions, molecular bands, and continuous background radiation. The intensities of the spectral lines are related to the laser energy used to create the plasma and the detection system.

The Experimental Procedure

The laser energy (Applied Spectra Model RT100-B) was adjusted to obtain sufficient peak power needed to form plasma. The laser operating at 266 nm wavelength was employed as an excitation source delivers pulse energy of 80 mJ. The sample was put in the sample cell and irradiated with delay time 0.5ns. The emission spectra were collected via a fiber optic to the spectrometer, spectrometer was connected to the PC through USB cable. The displayed LIBS spectra of the sample were identified with different intensities in the recorder by referring to the NIST atomic spectra database and references. These steps was applied to all the samples.

III. Results and Discussion

Figures (1-9) show the LIBS emission spectra for the sample in the range of (100 -1100) nm recorded at delay time of 0.5ns and laser pulse energy 80 mJ. Tables(2-10) list the analysis of the wavelengths corresponding to different elements and their intensities in the nine samples.

Results of the water bottles samples before use:**Figure 1.** LIBS emission spectrum of sample (M11).**Table (2)** The analyzed data of sample M11, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u)	Elements
272.121	5809	Mn II
491.773	4213	Ca I
547.361	1961	Cl II
499.547	162	S II
566.663	934	N II
612.027	713	K II
690.982	1405	F II

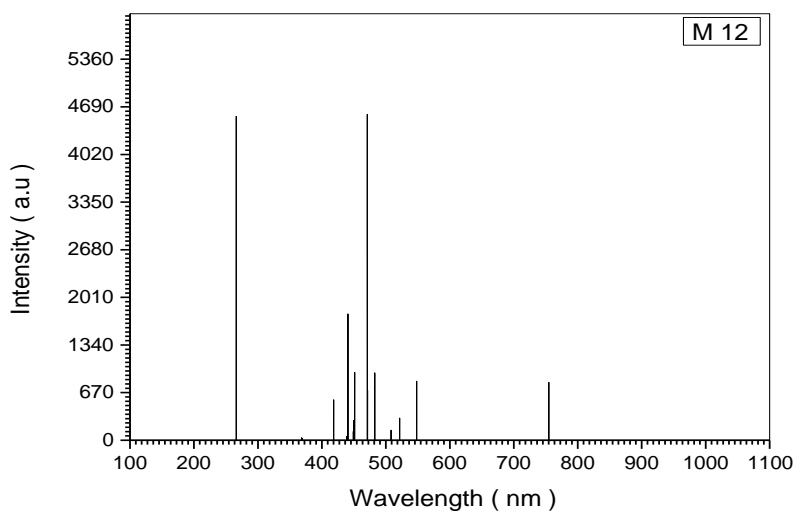


Figure 2. LIBS emission spectrum of sample (M12).

Table (3) The analyzed data of sample M12, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
268.824	4620	Mn I
422.672	637	Ca I
442.541	1814	Ca I
457.110	975	Mg I
476.864	4606	Cl I
480.328	940	N II
507.829	153	Cl II
521.155	311	Sc I
547.362	845	S II
755.223	817	F I

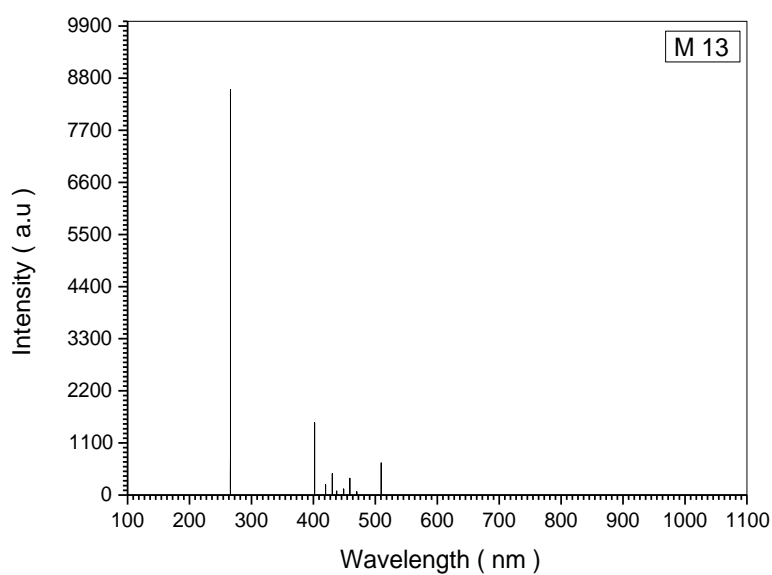


Figure 3. LIBS emission spectrum of sample (M13).

Table (4) The analyzed data of sample M13, irradiated by 80 mJ

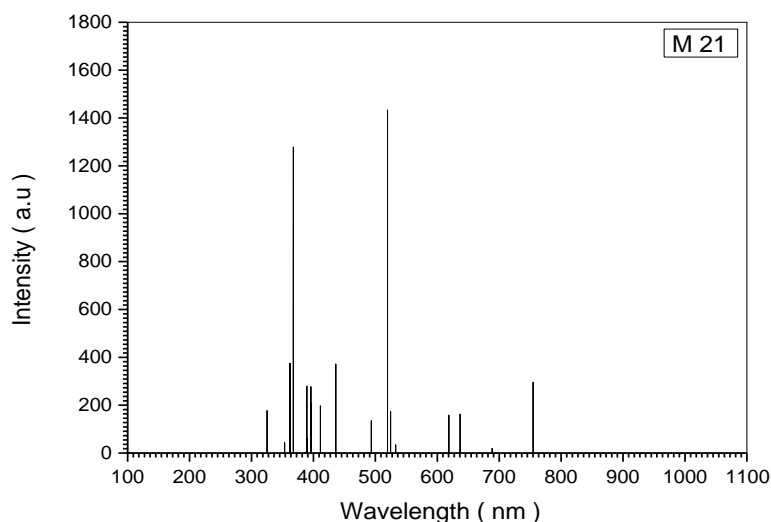
Measured λ (nm)	Intensity (a.u)	Elements
268.824	8516	Mn I
422.672	1551	F I
402.473	278	Ca I
430.771	517	Ca I
457.133	374	Mg I
507.829	711	Cl II

Figures (1-3) illustrate the spectra of elements present in the water bottles samples before use. Tables(2-4) show the existing elements in the samples, their wavelengths, and their intensities.

For all samples the detection limit is (200 – 1150 nm) according to detector sensitivity it was out ranged of the main element's that made for water containers polyethylene terephthalate (PET) (C and H) element in the ranged before 200 nm for this response these two elements were not found on the results.

For LIBS spectrum of the first group (M11, M12 and M13), for water bottle before use, the most sensitive lines (finger print wavelength) for identification of elements were found by using NIST database the elements (Mn II, Ca I, Cl II, S II, N II, K II, and F II), For M 11 sample, (Mn I, Ca I, Cl I, Mg I, N II, S II, Sc I and F I), for M 12 sample and (Mn I, Ca I, Cl II, Mg I and F I), for M13 sample. Most of these elements are in agreement with the results of previous studies published in scientific literature [12,13], except for the elements (Cl II, F II) that were first observed. This group are useful for recycling only once time.

Results of the water bottles samples after use:

**Figure 4.** LIBS emission spectrum of sample (M21).**Table (5)** The analyzed data of sample M21, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u)	Elements
325.295	186	Mn I
370.633	368	Ca II
373.690	1301	Ca II
396.877	275	Ca II
413.247	203	Cl II
435.119	74	Mg I
496.392	147	N I
518.808	1447	Ca II
524.616	1456	Pm II
615.818	186	O II
634.851	170	F I
755.224	301	F I

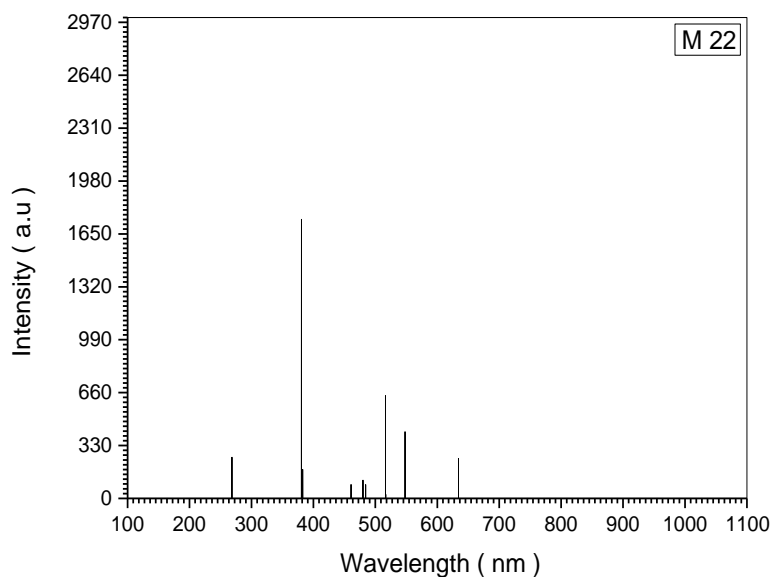


Figure 5. LIBS emission spectrum of sample (M22).

Table (6) The analyzed data of sample M22, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u.)	Elements
268.921	286	Fe I
373.670	1745	Ca II
460.845	82	K II
480.327	124	N II
487.885	95	Ca I
518.363	640	Mg I
545.702	424	Cl II
634.851	250	F I

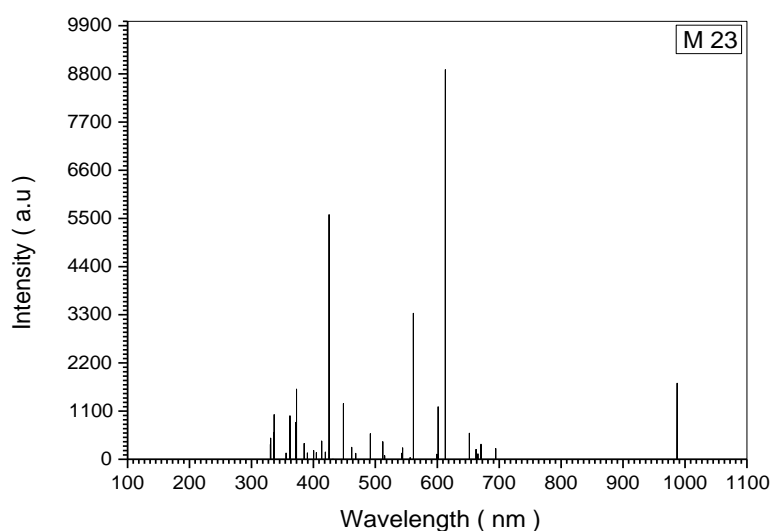


Figure 6. LIBS emission spectrum of sample (M23).

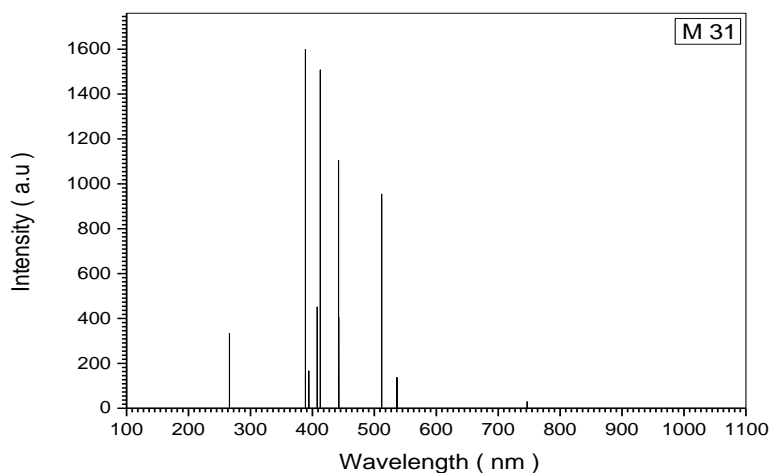
Table (7) The analyzed data of sample M23, irradiated by 80mJ

Measured λ (nm)	Intensity (a.u)	Elements
331.235	518	Er II
336.827	1083	Mo I
361.848	1024	K II
370.601	1648	Ca II
424.179	5683	N II
444.779	1264	F II
491.772	591	Cl II
511.226	398	K I
571.121	330	Mg I
600.973	1144	Eu I
612.024	8876	K II
654.595	582	Mg II
989.062	1744	Ca II

Figures 4-6 illustrate the spectra of elements present in water bottle samples after use. Tables 5-7 show the elements present, their wavelengths and their intensity.

For all samples the detection limit is (200 – 1150 nm) according to detector sensitivity it was out ranged of the main element's that made for water containers polyethylene terephthalate (PET) (C and H) element in the ranged before 200 nm for this response these two elements were not found on the results.

For LIBS spectrum of second group (M21, M22 and M23), water bottles after use are (Mn I, Ca II, Cl II, Mg I, N I, Pm II, O II and F I) for M21, (Fe I, Ca II, Cl I, Mg I, K II, NII and F I) for M 22 and (Er II, Mo I, Ca II, Cl II, Mg I, K II, N II, Eu I and F II) for M23 and also all elements are agree with the results of previous studies [2,13,14], except (Cl II, F II) the spectra showed lines corresponding to elements that have not been observed by other techniques, such as Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectroscopy (AAS), this elements group was normal and useful for recycling only once time.

**Figure 7.** LIBS emission spectrum of sample (M31)**Table (8)** The analyzed data of sample M 31, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u)	Elements
268.921	329	Mo I
386.097	1603	Cl II
393.347	157	Ca II
404.176	444	N II
410.386	1502	F II
448.113	1108	Mg II
511.228	963	K II
539.212	146	Cl II

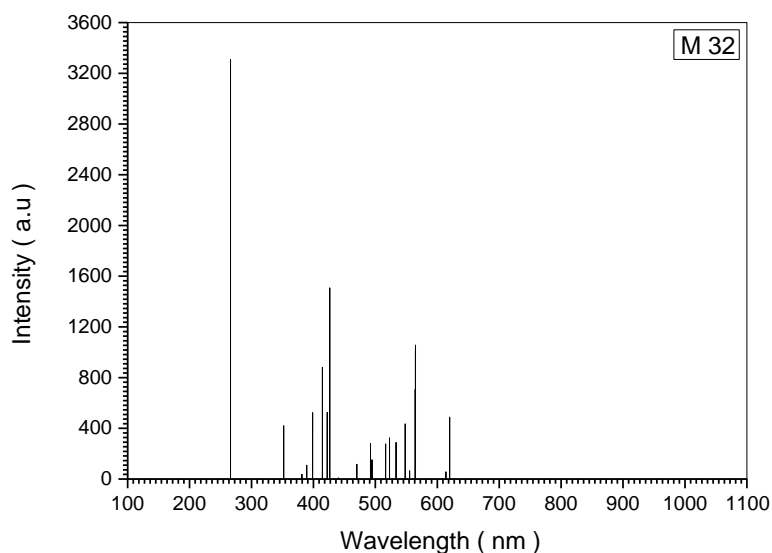


Figure 8. LIBS emission spectrum of sample (M32)

Table (9) The analyzed data of sample M 32, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u)	Elements
268.977	3310	Fe I
353.073	455	K II
393.364	110	Ca II
398.848	520	Ca II
413.249	908	Cl II
424.133	520	N II
424.623	1225	F II
457.109	120	Mg I
533.969	316	K I
545.702	430	Cl II
563.997	1018	S II
623.964	522	F I

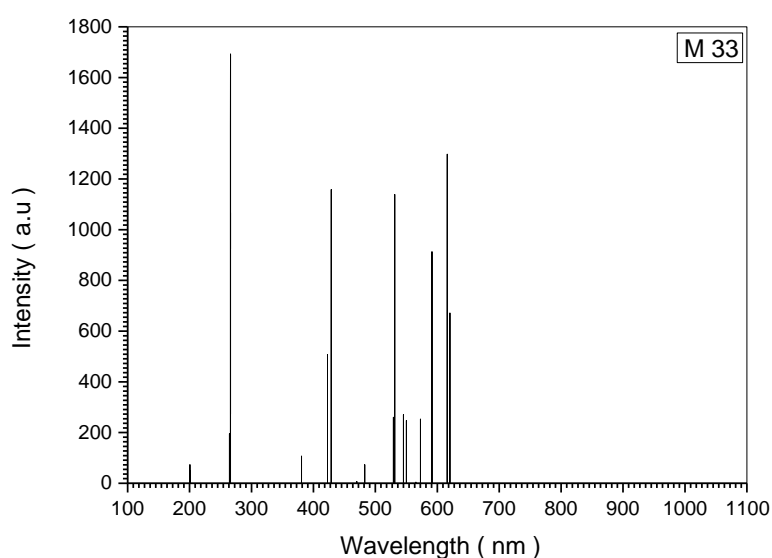


Figure 9. LIBS emission spectrum of sample (M33)

Table (10) The analyzed data of sample M 33, irradiated by 80 mJ

Measured λ (nm)	Intensity (a.u)	Elements
199.719	88	Mn I
268.921	1705	Fe I
373.674	130	Ca II
424.183	502	N I
424.623	1157	F II
481.947	82	Cl II
532.328	1168	K I
545.702	262	Cl II
547.362	250	S II
571.037	268	N I
593.175	917	N II
615.423	1307	Na I
623.965	676	F I

Figures 7-9 show the spectra of the elements in water bottle caps samples. Tables 8-10 show the elements present, their wavelengths, and their intensity.

For all samples the detection limit (200 – 1150) according detector sensitivity it was out ranged of the main element's that made for water bottle caps high density polyethylene(HDPE) (C and H) element in the range before 200 nm for this response these two elements were not found on the results.

The last group, it is of water bottle caps (M31, M32 and M33) the finger print wavelength are (Mo I, Ca II, Cl II, Mg II, N II, K II, and F II) for M31 sample, (Fe I, Ca II, Cl II, Mg I, N II, K II, S II and F I) for M32 sample and (Fe I, Ca II, Cl II, Mn I, N II, K I, S II, Na I and F I) for M33 sample, and also all elements were normal. Although there are a heavy metals, but it usually found at trace levels, such as Fe and Mo.

IV. Conclusions:

Laser induced breakdown spectroscopy (LIBS) is useful technique for analyses the plastic water bottles samples and this technique led to accurate determination of different elements. The pulse energy irradiated to the samples at 80mJ were suitable to detect high amounts of elements.

All elements present in plastic water bottles were detected using laser induced breakdown spectroscopy RT-100B, The elements that detected are (Mn II, Ca II, Cl II, S II, N II, K II, Mg I, Pm II, O II, Mo I, Mg II and F II). present in plastic water bottles samples were estimated and results achieved are in good agreement and all these elements are normal and this groups are useful for recycling only once time.

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