



# Identification of Microplastics in Plastic Bottled Drinking Water Using Laser-Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy

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## Authors' contributions

This work was carried out in collaboration among all authors. Author BOO carried out sample preparation, lab experiments and data analysis. Author JOG edited the manuscript and provided supervisory roles. Author RN did experimental setup and provided supervisory roles on the development of the manuscript. Author WNO helped in acquisition of samples, provided technical assistance and professional advice in the development of this work. All authors read and approved the final manuscript.

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## ABSTRACT

Microplastics contamination in drinking water is a growing concern globally as reported in recent papers. Here we report an investigation on the identification and classification of microplastics present in bottled drinking water using Laser induced breakdown spectroscopy, and Raman

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spectroscopy. Different brands of bottled drinking water from different manufacturers were sampled for this investigation in Kenya. Rapid classification and identification of microplastics polymer types presence in the sampled water was done with Laser-Induced Breakdown Spectroscopy, and Raman Spectroscopy. The two techniques were used to determine molecular and atomic information of various MP polymers detected using scattered signal and plasma spectra. Five polymers polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC) were successfully detected and identified in the sampled water. Among the five polymers, the most common was PE, which was observed in 5 out of the 14 samples (35.71%). The second most dominant polymer was PET, which was detected in 4 out of the 14 samples (28.57%). Three polymers, PS (14.28%) and PP (14.28%) were detected in 2 out of 14 samples each, while PVC (7.14%) was identified in 1 sample. All the particles detected had sizes ranging between 20  $\mu\text{m}$  to 70  $\mu\text{m}$ . The findings clearly demonstrate possible contamination of bottled drinking water with microplastics. Raman spectroscopy and Laser Induced Breakdown spectroscopy (LIBS) are promising techniques for detection and identification of microplastics in bottled drinking water.

*Keywords: Bottled drinking water; laser-induced breakdown spectroscopy; microplastics; polymers; Raman spectroscopy; spectroscopy.*

## 1. INTRODUCTION

Water is a crucial resource that has a significant impact on human well-being and is an essential part of our daily life. Most governments prioritize providing their citizens with safe and clean drinking water, and some have succeeded in doing so. However, in recent years, there has been a surge in the consumption of bottled drinking water, with average annual per capita global consumption reaching 329.33 billion liters [1]. While bottled drinking water is a popular choice, it is a cause for concern as it is less regulated than municipal tap water [2]. Most bottled water manufacturers use plastic as the preferred packaging material, which is often not recycled. Consequently, the plastic packaging ends up as landfill or litter in oceans and lakes, and over time breaks down into microplastics due to exposure to UV radiation, biofilm growth, mechanical shear, and wave action [3]. Microplastics can find their way into drinking water and their ingestion by humans poses serious health hazards such as cancer [4].

Microplastics can be classified in terms of size or origin. Depending on the size, they can be classified as small or large. Smaller microplastics have diameters ranging between 1  $\mu\text{m}$  to 1 mm [5]. Based on origin, microplastics can be classified as either secondary or primary. Secondary microplastics result from the breakdown of larger plastics due to continuous exposure to harsh environmental conditions. On the other hand, primary microplastics are those that are made intentionally by industries for use in cosmetic products and are usually in the micro

range [5]. Microplastics can accumulate toxic substances such as hard metals which are known to cause cancer and endocrine disruption thus affecting the overall human health [6] [7]. Recent works have pointed out the presence of microplastics in various places, not limited to soil, human stool, and even the human placenta [5] [6] [7]. There is little work that has been done to establish the presence of microplastics in bottled drinking water globally.

Several methods have been used to detect and identify microplastics in oceans, lakes, underground water and other water bodies. Some techniques that have been used include FTIR, NIR, Raman, SEM-EDS, NMR, and photoluminescence [5]. The FTIR technique utilizes the interaction between the sample and IR radiation to determine the molecular structure. This method is nondestructive, reliable, and direct [8]. However, this technique is limited as its efficiency is highly reduced due to the irregularity of the particles in the reflection mode. It works well for dry samples only and is limited to particles with sizes greater than 10 microns [9]. The NIR method also identifies materials by analyzing the produced molecular vibrations from the sample being shone with electromagnetic radiation. This method provides a greater penetration power, and there is less sample preparation than FTIR. However, it is limited to particles with diameters greater than 1 mm [5]. A recent technique that has been applied in the identification of microplastics is Photoluminescence spectroscopy which is based on the principle that all optically excited materials emit electromagnetic radiation on return to the

ground state. This method has shown its prowess by distinguishing between plastic and non-plastic materials [10]. However, this method is affected by an overlap of some bands, thus making it quite challenging to distinguish between different kinds of plastics [10]. The demerits of the existing techniques necessitate for a development of a technique that can be reliable and have the ability to be used in-situ studies.

There are limited studies focusing on the use of LIBs and Raman Spectroscopy together in the identification of microplastics. Raman spectroscopy is a molecular analysis technique that works on the principle of inelastic light scattering. This method provides the ability to determine the chemical structure and identify the constituent particles of a sample [11]. This method has been widely used in the identification of microplastics thanks to its high sensitivity to non-polar functional groups, high resolution for smaller particles, and little interference from water [5]. Laser-induced breakdown spectroscopy (LIBS) on the other hand is an elemental analysis technique that uses laser ablation to develop plasma on the surface of a sample. As the plasma containing the excited atoms or ions cools down, it releases electromagnetic radiations specific to a given element. This method has been used to identify polymers by analyzing the line intensity ratios of carbon and hydrogen [12] [13] [14]. Polymers have also been recognized by analyzing molecular information such as the  $C_2$  Swan bands [12] [15].

Combining the two techniques provided the analyzed microplastic's elemental, molecular, and structural information. Raman spectroscopy requires rapid sample preparation, which is quite time-consuming, whereas LIBS, on the other hand, requires no or little sample preparation [9]. Combining the two techniques thus enables them to complement each other and increase the level of accuracy. Few studies have employed a Raman-LIBS hybrid system for sample analysis [16] [17]. This study used LIBS elemental signals of the various samples, which were then compared with Raman spectroscopy signals for the complete identification of microplastics. Few studies have also reported applying the LIBS technique and Raman spectroscopy on the same sample [17]. In this study, we have utilized Raman and LIBS spectroscopy techniques to detect and identify microplastics in bottled water samples.

## **2. MATERIALS AND METHODS**

### **2.1 Water Samples**

All the water samples used in this study, were collected from various outlets in Narok and Nairobi counties, Kenya. For each sample, 1.5 L of plastic bottled water was bought from local vendors, and a total of fourteen samples were used. Each sample belonged to a different manufacturing plant.

### **2.2 Experimental Procedure**

#### **i. Raman Measurements**

One liter of each water sample was filtered under normal conditions through a Whatmann 1442-0.70 quantitative filter paper, ashless grade 42, 70 mm diameter, 200 microns thickness, 2.5 microns retention rate, ash content of <0.007% and filtration rate of 1870 seconds/100 ml of water. The filter paper was then placed in a sterilized petri dish and left to dry overnight at room temperature. The Raman system was calibrated using a silicon wafer and adequately aligned to the  $520.5\text{ Cm}^{-1}$  spectra. The vibrational spectra of the microplastics were measured using an STR Raman spectrometer manufactured by Seki Technotron Japan. The Laser Quantum gem, He-Ne 532 nm wavelength, 721 nm laser spot size with a resolution of  $2.0\text{ Cm}^{-1}$  having a frequency range of  $50\text{-}4000\text{ Cm}^{-1}$  was used as an excitation source for the Raman System. The 532 nm laser was chosen because the wavelength of excitation and the Raman scattering intensity is proportional to each other; hence using a shorter wavelength improves the overall sensitivity of the Raman system. The system had Raman optics consisting of 532 nm filters, properly aligned mirrors, 50/50 beam splitters, and a neutral density filter, all provided by Seki Technotron Japan. The system incorporated a confocal Raman Optical Microscope BX51 made by Olympus. All samples were viewed under an objective lens of 100x and a numerical aperture of 0.90, providing a resolving power of 0.00384 with a power delivery of 1.886 mW. Raman imaging was done with an Acton SP2300 with a 0.300 m triple grating monochromator made by Princeton Instruments. For this work 600 Blz grating was used with A Pixis 256 detector to collect the Raman signal. The sensor was operated at  $-75\text{ }^\circ\text{C}$ , and an ARix Corp STR Raman software version 1.41.3 was used for system operation. Three particles were

viewed under a 100x lens, their sizes were measured using Raman spectrometer measuring tool and five spectra were measured randomly across each particle for spectral analysis. For each spectrum to be obtained the particle was exposed to a laser beam for 10 sec with an acquisition mode set to five accumulations for each measurement. The obtained spectra were then analysed to identify the detected microplastics.

## ii. LIBS Measurements

For LIBS measurements, the bulky method proposed by [18] was used which enables direct water sample analysis for the detection of microplastics. Accurate volumetric measurements were done using a glass beaker that was thoroughly rinsed with deionized water. 100 ml of each sample was poured into a glass holder, and a laser beam was directly shone on it to collect spectra. Laser-induced breakdown spectrometer (LIBS) was used to do the elemental analysis for the sampled water for the detection of microplastics. The LIBS spectrometer by Ocean Optics was employed in this analysis. The Ocean Optics LIBS2500 plus spectrometer system was used with a Q-switched Big Sky Quantel laser having a center wavelength of 1064 nm. The laser energy was set to 250 mJ with a pulse width of 8 ns and a pulse repetition frequency of (PRF) of 1 Hz. For each pulse, the Laser provided a peak power of 31.25 mW with a period of 1s. This system allowed qualitative elemental measurements in real-time. The spectra were analysed between 200-980 nm wavelength providing a resolution of ~0.1 nm (FWHM). The system had seven spectrometer channels ranging between 198.16 – 971.11 nm wavelength. The results were evaluated using OOILIBSplus application software version 4.5.0.7 provided by Ocean Optics. The software allowed the identification of emission lines for the various elements, correlation of the background signal, monitoring of the emission spectra, data logging, spectral saving, and Laser firing in the operation of the LIBS2500 plus system. The LIBS also contained a spectral library with 2500 atomic emission lines obtained from the National Institute of Standards and Technology (NIST). The emission lines aided with the identification and calibration of the LIBS 2500 Plus system. For each sample, 200 spectra were taken randomly and analysed individually. The holder was then rinsed again before placing another water sample. The procedure was repeated four times for each

sample until all fourteen samples were measured.

## 3. RESULTS AND DISCUSSION

The measured spectra were analysed for the identification of the microplastics. The vibrational spectra obtained from the Raman measurements indicated the presence of specific polymers in the water samples for the identification of the microplastics. The atomic spectra obtained from the LIBS measurements were used to determine the C/H ratios of the polymers for the detection of MP in sampled water. The target polymers for identification were both aromatic (PS) and aliphatic (PE, PP, PVC, PET) [15] which are major packaging polymers for the bottled water.

Fig. 1 shows Raman and atomic spectra for five out of the fourteen samples, Raman bands that were observed at  $1063\text{ cm}^{-1}$  and  $1129\text{ cm}^{-1}$ , are associated with the stretching of the C-C bond,  $1169\text{ cm}^{-1}$ , which is associated with  $\text{CH}_2$  rocking vibration,  $1291\text{ cm}^{-1}$ , which is as a result of  $\text{CH}_2$  twisting vibration,  $1442\text{ cm}^{-1}$   $\text{CH}_2$  bending vibration,  $2850\text{ cm}^{-1}$  which is the Symmetric stretching of  $\text{CH}_2$  and  $2884\text{ cm}^{-1}$  which is from Asymmetric stretching of  $\text{CH}_2$  vibration as presented in Fig. 1(a). The observed bands are characteristic of Polyethylene [19] [20] [21] [22]. Fig. 1(b) represents the atomic spectra obtained from LIBS for the five samples. The average C/H ratio for the five samples was 1.56. The high C/H value is as a result of higher density which results from the level of crystallinity of PE and is close to what was obtained by [13] which further indicates the presence of polyethylene.

Fig. 2 also shows Raman and Laser induced breakdown spectra for four out of the fourteen water samples, Raman bands were observed at  $858\text{ cm}^{-1}$ , which is a result of the stretching vibrations of C-C and C-(O)-O bond,  $1096\text{ cm}^{-1}$ , which is due to the antisymmetric stretching vibrations of C-O-C,  $1118\text{ cm}^{-1}$  which is associated with C-C bonds of ethylene glycol and C(O)-bond,  $1185\text{ cm}^{-1}$  due to the stretching vibrations of the C-C bond,  $1295\text{ cm}^{-1}$  which results from the stretching vibrations of C(O)-O bond,  $1420\text{ cm}^{-1}$  which comes from the bending vibrations of O-CH,  $\text{CH}_2$  and C-CH bonds,  $1615\text{ cm}^{-1}$  which results from vibrations of the ring mode 8a in the Wilson notation and  $1739\text{ cm}^{-1}$  which arise from the stretching vibrations of C=O. The observed Raman bands are presented in Fig. 2(a). The observed bands are characteristic of Polyethylene Terephthalate [17]

[19] [23]. The LIBS atomic spectra for the four samples are presented in Fig. 2(b). The average C/H ratio obtained for the four samples was 1.11 which is closer to what was obtained by [13] [14] and this further indicates the presence of polyethylene Terephthalate in the sample.

In two out of the fourteen samples Raman bands were observed at  $398\text{ Cm}^{-1}$ , which is due to the bending of the CH and wagging of the  $\text{CH}_2$  bonds,  $809\text{ Cm}^{-1}$ , which is due to rocking vibrations of  $\text{CH}_2$ , C-C, and C- $\text{CH}_3$  bonds stretching vibrations,  $841\text{ Cm}^{-1}$  which result from rocking vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  and the stretching vibrations of C- $\text{CH}_3$  and C-C bonds,  $984\text{ Cm}^{-1}$  which results from rocking vibrations of  $\text{CH}_3$  and stretching vibrations of C-C bonds. The  $1040\text{ Cm}^{-1}$  results from the stretching vibrations

of C- $\text{CH}_3$  and C-C bonds and the bond CH's bending vibrations. The band at  $1164\text{ Cm}^{-1}$  is due to CH bending and  $\text{CH}_3$  rocking vibrations; other notable Raman bands occurred at  $1320\text{ Cm}^{-1}$  and  $1468\text{ Cm}^{-1}$ , which result from twisting of  $\text{CH}_2$ , bending vibrations of CH, Asymmetric bending of  $\text{CH}_3$  and bending vibrations of  $\text{CH}_2$ . The observed Raman bands are presented in Fig. 3(a). These Raman vibrational bands are characteristic of Polypropylene [17] [19] [24] [25] [26]. Fig. 3(b) presents the atomic spectra for the LIBS measurements. The average C/H ratio for these two samples was found to be 1.17. PP contains methyl groups and substituted methylene groups which are the repeating units. The obtained ratio differs closely to what was obtained by [12] and [13] which is characteristic to Polypropylene.

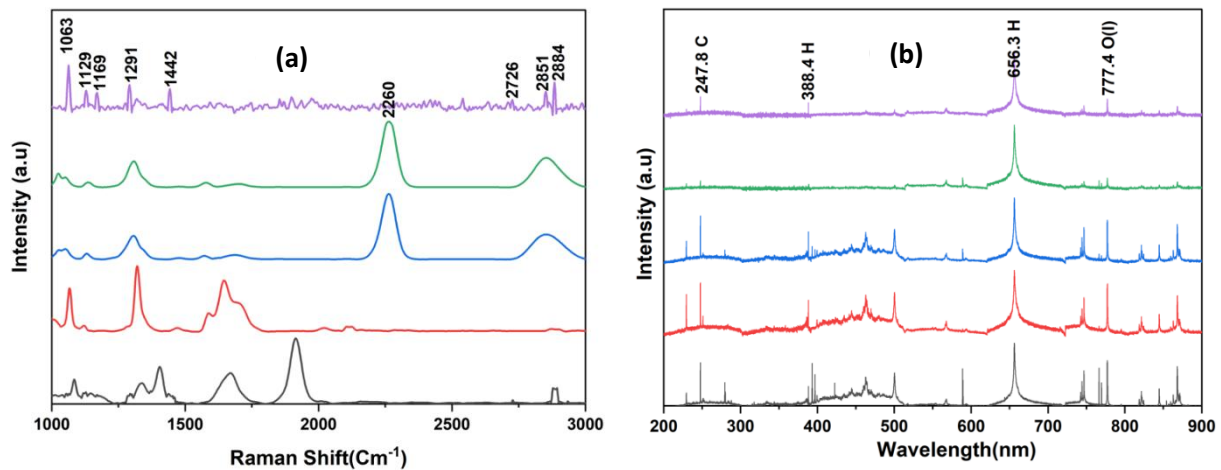


Fig. 1. (a) Raman Spectra and (b) LIBS spectra for samples containing polyethylene

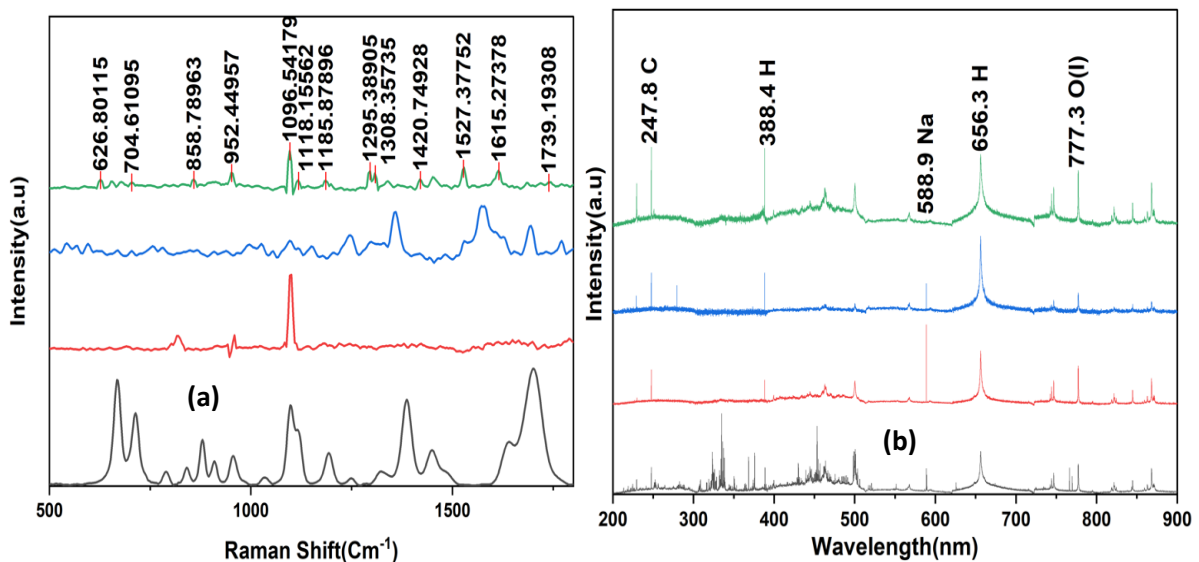
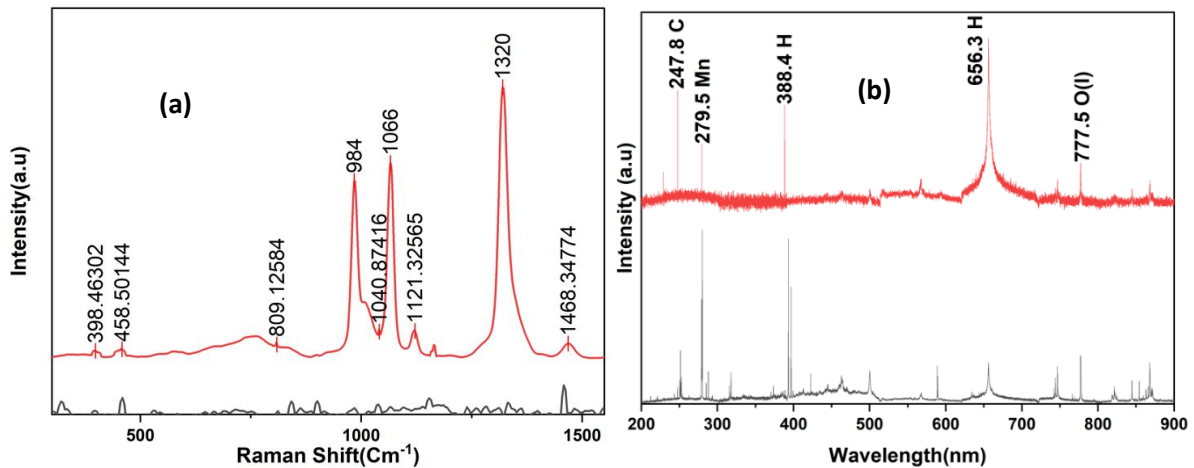


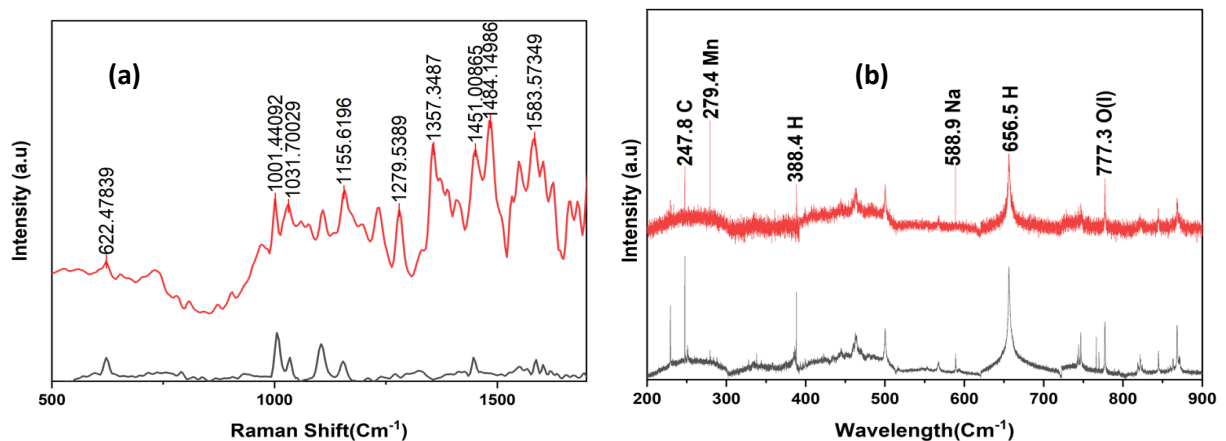
Fig. 2. (a) Raman spectra and (b) LIBS spectra for samples containing PET



**Fig. 3. (a) Raman spectra and (b) LIBS spectra for samples containing PP**

In another two out of fourteen samples, Raman bands were observed at  $622\text{ Cm}^{-1}$ , which is due to the ring deformation mode, a dominant peak at  $1001\text{ Cm}^{-1}$  which arises from the ring breathing mode of the aromatic carbon ring,  $1031\text{ Cm}^{-1}$  band, which is assigned to in-plane CH deformation,  $1155\text{ Cm}^{-1}$  which comes from the stretching vibrations C-C,  $1451\text{ Cm}^{-1}$  set to the scissoring vibrations of  $\text{CH}_2$  and  $1602\text{ Cm}^{-1}$  that results from the stretching vibrations of the ring skeletal. The observed bands are depicted in Fig. 4(a). These vibrational spectra are characteristic of polystyrene (PS) [17] [19] [27]. The LIBS spectra of the two water samples are shown in Fig. 4(b). The average C/H ratio was found to be 1.40 which is in agreement with [13] and further indicates the presence of Polystyrene.

In one of the water samples, Raman bands were observed at  $361\text{ Cm}^{-1}$ , which is a result of the trans configuration of the C-Cl bond in the PVC polymer,  $612\text{ Cm}^{-1}$  assigned to Stretching of C-Cl,  $695\text{ Cm}^{-1}$ , which is due to the stretching vibrations of C-Cl bonds,  $1395\text{ Cm}^{-1}$  which results from C-H symmetrical stretching in the  $\text{CH}_2$  group,  $1430\text{ Cm}^{-1}$  which is due to the stretching of C-C bond. The bands are shown in Fig. 5(a). These peaks are characteristic of the PVC molecule [28] [29]. PVC contains many additives, which explains the unidentified Raman bands [19]. Fig. 5(b) presents the obtained LIBS spectra for the sample whose average C/H ratio was 0.89. The obtained value is close to what was obtained by [13] [14] which further indicate the presence of Polyvinyl Chloride (PVC).



**Fig. 4. (a) Raman spectra and (b) LIBS spectra for samples containing PS**

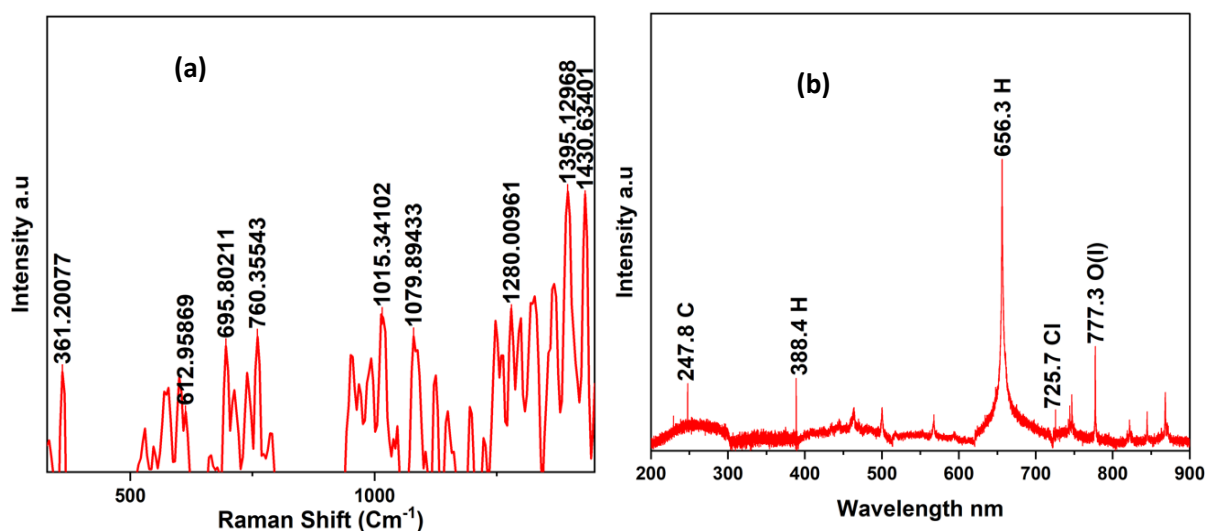


Fig. 5. (a) Raman spectra and (b) LIBS spectra for samples containing PVC

Table 1. Atomic spectra lines that were identified in the LIBS spectra

Element	$\lambda$ (nm)	Transition	Reference
C	247.8	$2s^22p^2-2s^22p^3s$	[12] [15] [30]
H	388.4	Signature emission for H	[12] [13]
Na	588.9	Signature emission for Na	[12] [13]
H	656.3	$n = 3 \rightarrow 2$ (Balmer- $\alpha$ )	[15] [30] [31]
Cl	725.7	Signature line for Cl	[15] [14]
O(I)	777.3	$2s^22p^33s-2s^22p^33p$	[12] [15]

Table 1 summarizes the identified atomic spectra lines from the LIBS measurements at different characteristic wavelengths. These spectral lines were specifically chosen because their intensity was higher enough and thus the interference from other emission lines was highly reduced. The lines also do not involve the ground state and thus self-absorption is negligible. For the LIBS measurements the emission line at 247.8 nm corresponds to an electronic transition from  $2s^22p^2$  to the  $2s^22p^3s$  state. The emission line at 388.4 nm is a signature emission line for Hydrogen atom. The atomic emission line at 656.3 nm is a representation of the Balmer lines which arise from the transition of the H atoms from energy level 3 to energy level 2. The Cl line is seen specifically for PVC at 725.7 nm [15]. The emission line at 777.3 nm represents O(I) atom that is transitioning from  $2s^22p^33s$  state to the  $2s^22p^33p$  state. Lastly, the detected emission line at 588.9 nm and 279.4 nm which is a signature for Na and Mn respectively and thus indicating the ability of LIBS to detect trace elements [12] [13] [14] [15]. The electronic transitions for the

various elements that were detected in the microplastics are as shown in Table 1.

#### 4. CONCLUSION

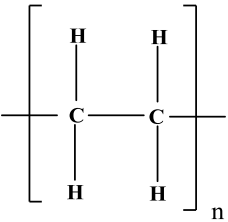
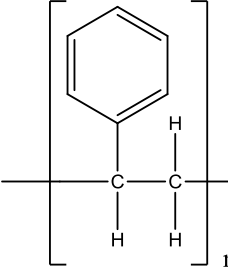
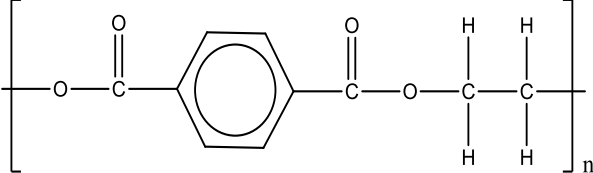
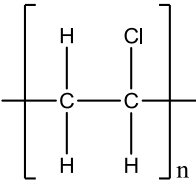
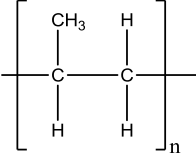
This work has successfully applied Raman and LIBS techniques to identify microplastics present in bottled drinking water with the smallest particle being 20  $\mu\text{m}$  and the largest being 63.4  $\mu\text{m}$ . Out of the 14 samples, PE was found in five samples, PET in four samples, PS and PP in two samples each, and PVC in one sample. The study's findings indicate that PE is the most common polymer in bottled drinking water. From the LIBS measurements, the average C/H ratios for the five samples were PE (1.56), PET (1.11), PS (1.40), PP (1.17), and PVC (0.89). The observed average C/H ratio trend was PE > PS > PP > PET > PVC. The ratios can be assumed to be characteristic of the presence of the polymers in water samples. The obtained results prove that the combination of Raman and LIBS techniques offers a rapid and efficient alternative for microplastic detection. The two approaches are



nondestructive, reliable, and can be used in situ measurements. They have high resolution to smaller particles; hence they can be used to detect small particle sizes. The techniques are also sensitive to non-polar functional groups and experience little interference from water samples. This study can guide future research on the identification and classification of microplastics. Microplastics have also been shown to have various health effects that are detrimental to

human health. Detection and identification are essential in the whole process of minimizing their health effects. Therefore, the techniques explored in this current study can be applied in industrial contexts to detect and identify microplastics. Their application will ensure the manufacture of safe drinking water that does not pose health risks. The possible human health effects caused by microplastics are summarized in the Table 2.

**Table 2. Table showing structure, uses and potential health effects of the detected species**

Polymer	Structure	Application	Health Effects
PE		Plastic wrap Toothpaste	Liver damage [32]
PS		Packaging Single-use coffee cups.	Liver inflammation [33] Can cause apoptosis in human cells [34]
PET		Water bottles Plastic bags Plastic packaging	Can cause microbiota dysbiosis [34]
PVC		Water pipes Floor tiles Packaging	Alter the genes [13] Carcinogenic [4]
PP		Packaging Clothing (laboratory)	Can induce cytokines that cause inflammation [35]



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## COMPETING INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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