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

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Original Research Article

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 μm to 70 μm. 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.

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 μm 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 Cm^{-1} spectra. The vibrational spectra of the microplastics were measured using an STR Raman spectrometer mmanufactured by Seki Technotron Japan. The Laser Quantum gem, He-Ne 532 nm wavelength, 721 nm laser spot size with a resolution of 2.0 Cm^{-1} having a frequency range of 50-4000 Cm^{-1} was used 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 ^{o}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 Cm^{-1} and 1129 Cm^{-1}, are associated with the stretching of the C-C bond, 1169 Cm^{-1}, which is associated with CH_2 rocking vibration, 1291 Cm^{-1}, which is as a result of CH_2 twisting vibration, 1442 Cm^{-1} CH_2 bending vibration, 2850 Cm^{-1} which is the Symmetric stretching of CH_2 and 2884 Cm^{-1} which is from Asymmetric stretching of 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 Cm^{-1}, which is a result of the stretching vibrations of C-C and C-(O)-O bond, 1096 Cm^{-1}, which is due to the antisymmetric stretching vibrations of C-O-C, 1118 Cm^{-1} which is associated with C-C bonds of ethylene glycol and C(O)-bond, 1185 Cm^{-1} due to the stretching vibrations of the C-C bond, 1295 Cm^{-1} which results from the stretching vibrations of C(O)-O bond, 1420 Cm^{-1} which comes from the bending vibrations of O-CH, CH_2 and C-CH bonds, 1615 Cm^{-1} which results from vibrations of the ring mode 8a in the Wilson notation and 1739 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 Cm^{-1}, which is due to the bending of the CH and wagging of the CH_2 bonds, 809 Cm^{-1}, which is due to rocking vibrations of CH_2, C-C, and $C-CH_3$ bonds stretching vibrations, 841 Cm^{-1} which result from rocking vibrations of CH_2 and CH_3 and the stretching vibrations of $C-CH_3$ and C-C bonds, 984 Cm^{-1} which results from rocking vibrations of CH_3 and stretching vibrations of C-C bonds. The 1040 Cm^{-1} results from the stretching vibrations

of $C-CH_3$ and C-C bonds and the bond CH's bending vibrations. The band at 1164 Cm^{-1} is due to CH bending and CH_3 rocking vibrations; other notable Raman bands occurred at 1320 Cm^{-1} and 1468 Cm^{-1}, which result from twisting of CH_2, bending vibrations of CH, Asymmetric bending of CH_3 and bending vibrations of 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.
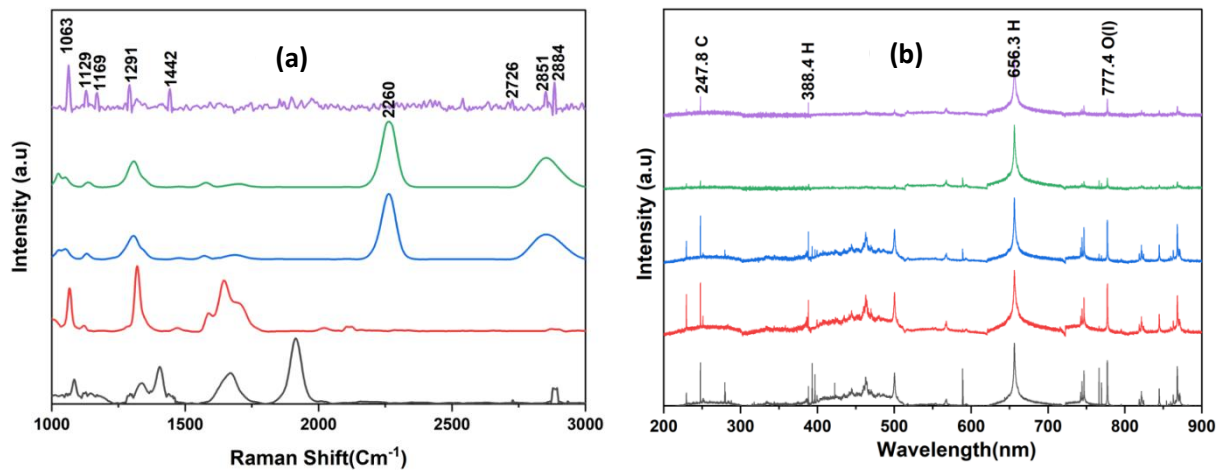

Fig. 1. (a) Raman Spectra and (b) LIBS spectra for samples containing polyethylene
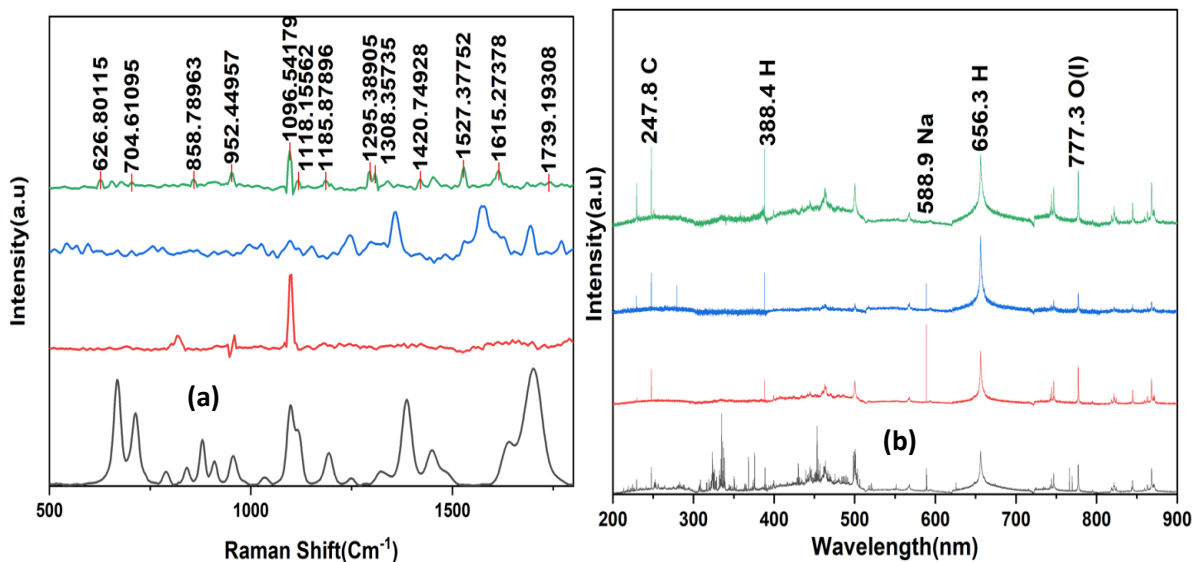

Fig. 2. (a) Raman spectra and (b) LIBS spectra for samples containing PET
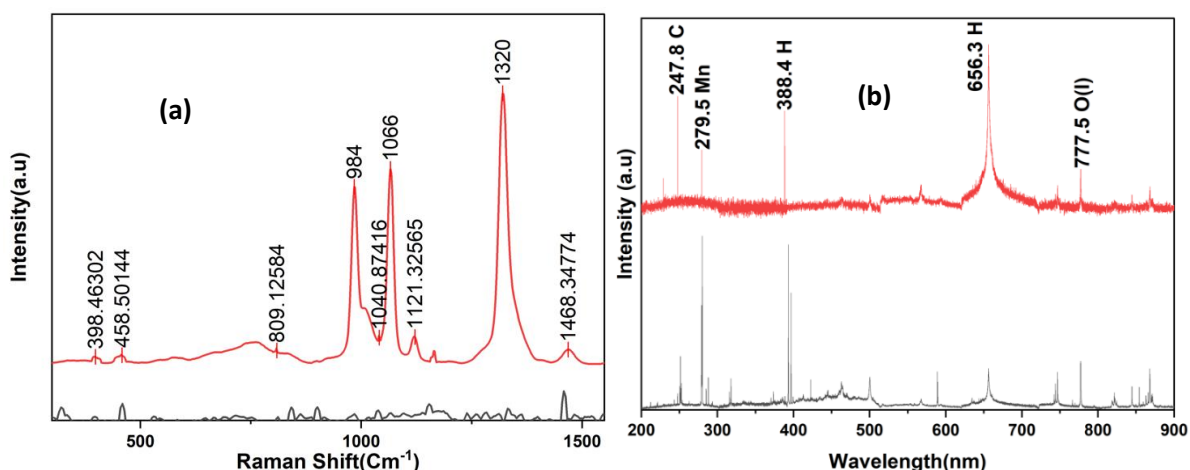
Fig. 3. (a) Raman spectra and (b) LIBS spectra for samples containing PP

In another two out of fourteen samples, Raman bands were observed at 622 Cm^{-1}, which is due to the ring deformation mode, a dominant peak at 1001 Cm^{-1} which arises from the ring breathing mode of the aromatic carbon ring, 1031Cm^{-1} band, which is assigned to in-plane CH deformation, 1155 Cm^{-1} which comes from the stretching vibrations C-C, 1451 Cm^{-1} set to the scissoring vibrations of CH_2 and 1602 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 Cm^{-1}, which is a result of the trans configuration of the C-Cl bond in the PVC polymer, 612 Cm^{-1} assigned to Stretching of C-Cl, 695 Cm^{-1}, which is due to the stretching vibrations of C-Cl bonds, 1395 Cm^{-1} which results from C-H symmetrical stretching in the CH_2 group, 1430 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).
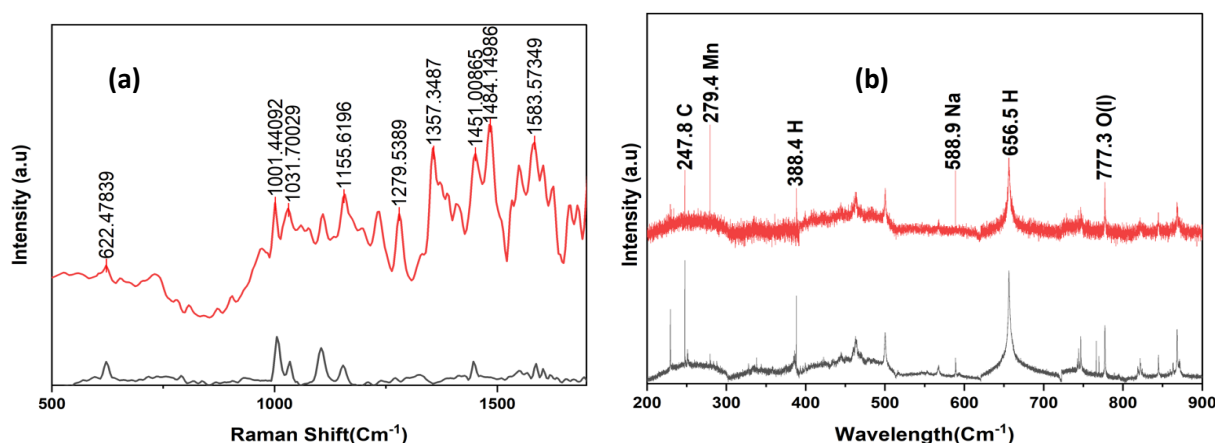

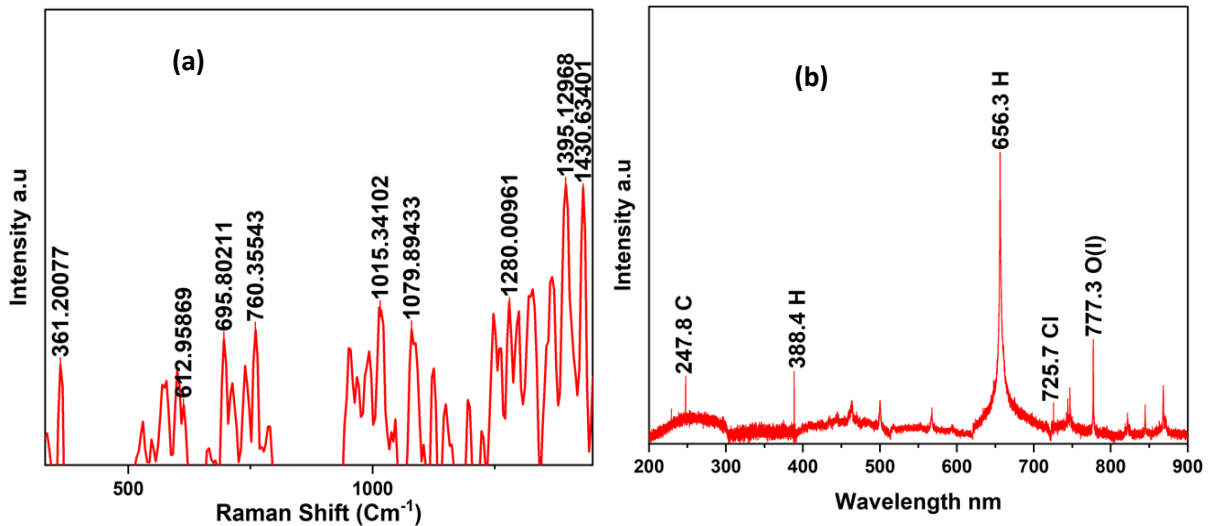**Fig. 4. (a) Raman spectra and (b) LIBS spectra for samples containing PS**

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	λ (nm)	Transition	Reference
C	247.8	$2s^2 2p^2 - 2s^2 2p^3 s$	[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-α)	[15] [30] [31]
Cl	725.7	Signature line for Cl	[15] [14]
O(I)	777.3	$2s^2 2p^3 3s - 2s^2 2p^3 3p$	[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 $2s^2 2p^2$ to the $2s^2 2p^3 s$ 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 $2s^2 2p^3 3s$ state to the $2s^2 2p^3 3p$ 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.
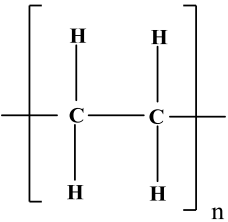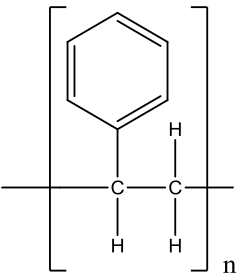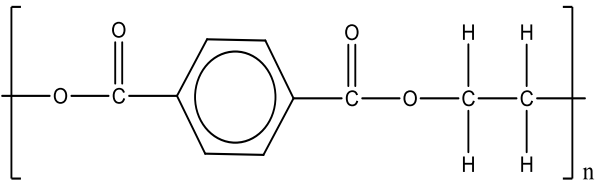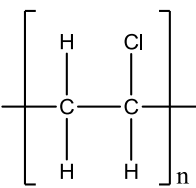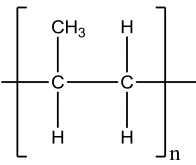
4. CONCLUSION

This work has successfully applied Raman and LIBS techniques to identify microplastics present in bottled drinking water with the smallest particle being 20 μm and the largest being 63.4 μm. 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.

REFERENCES

1. Qian N. Bottled water or tap water? A comparative study of drinking water choices on university campuses. Water. 2018;10(1):59.
2. Saylor A, Prokopy LS, Amberg S. What's wrong with the tap? Examining perceptions of tap water and bottled water at Purdue University. Environmental Management. 2011;48:588-601.
3. Andrady AL. The plastic in microplastics: A review. Marine Pollution Bulletin. 2017; 119(1):12-22.
4. Blackburn K, Green D. The potential effects of microplastics on human health: What is known and what is unknown. Ambio. 2022;51(3):518-530.
5. Tirkey A, Upadhyay LSB. Microplastics: An overview on separation, identification and characterization of microplastics. Marine Pollution Bulletin. 2021;170:112604.
6. Wright SL, Thompson RC, Galloway TS. The physical impacts of microplastics on marine organisms: A review. Environmental Pollution. 2013;178:483-492,.
7. Rochman CM, Hentschel BT, Teh SJ. Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. PLOS One. 2014;9(1):e85433.
8. Ojeda JJ, Romero-Gonzalez ME, Banwart SA. Analysis of bacteria on steel surfaces using reflectance micro-Fourier transform infrared spectroscopy. Analytical Chemistry. 2009;81(25):6467-6473.
9. Sommer C, Schneider LM, Nguyen J, Prume JA, Lautze K, Koch M. Identifying microplastic litter with Laser Induced Breakdown Spectroscopy: A first approach. Marine Pollution Bulletin. 2021; 171:112789.
10. Ornik J, Sommer S, Gies S, Weber M, Lott C, Balzer JC, Koch M. Could photoluminescence spectroscopy be an alternative technique for the detection of microplastics? First experiments using a 405 nm laser for excitation. Applied Physics B. 2020;126(1):1-7.
11. Araujo CF, Nolasco MM, Ribeiro AM, Ribeiro-Claro PJ. Identification of microplastics using Raman spectroscopy: Latest developments and future prospects. Water Research. 2018;142:426-440.
12. Eunok Kim, Woo Zin Choi. Real-time identification of plastics by types using laser-induced breakdown spectroscopy. Journal of Material Cycles and Waste Management. 2019;21(1):176-180.
13. Gondal MA, Siddiqui MN. Identification of different kinds of plastics using laser-induced breakdown spectroscopy for waste management. Journal of Environmental Science and Health, Part A. 2017;42(13):1989-1997.
14. Sattmann R, Moè Nch I, Krause H, Noll R, Couris S, Hatziapostolou A, Mavromanolakis A, Fotakis C, Larrauri E, Miguel R. Laser-Induced Breakdown Spectroscopy for Polymer identification. Appliedspectroscopy. 1998;52:0003-7028.
15. Grégoire S, Boudinet M, Pelascini F, Surma F, Detalle V, Holl Y. Laser-induced breakdown spectroscopy for polymer identification. Anal Bioanal Chem. 2011; 400:3331–3340.
16. Hoehse M, Paul A, Gornushkin I, Panne U. Multivariate classification of pigments and inks using combined Raman spectroscopy and LIBS. Anal Bioanal Chem. 2012; 402(4):1443-50.
17. Shameem KMM, Khoobaram S. Choudhari, Bankapur A, Kulkarni SD, Unnikrishnan VK, George SD, Kartha VB, Santhosh C. A hybrid LIBS–Raman system combined with chemometrics: an efficient tool for plastic identification and sorting. Anal Bioanal Chem. 2017;409:3299–3308.
18. Ruas A, Matsumoto A, Ohba H, Akaoka K, Wakaida I. Applcation of laser induced breakdown spectroscopy to zirconium in aqueous solution. Spectrochemistry Part B: Atomic Spectroscopy. 2017;131:99-106.
19. Nava V, Frezzotti ML, Leon B. Raman Spectroscopy for the Analysis of Microplastics in Aquatic Systems. Applied Spectroscopy. 2021;75(11):1341-1357.
20. Furukawa T, Sato H, Kita Y, Matsukawa K, Yamaguchi H, Ochiai S, Heinz. Siesler W,

Ozaki Y. Molecular Structure, Crystallinity and Morphology of Polyethylene/ Polypropylene Blends Studied by Raman Mapping, Scanning Electron Microscopy, Wide Angle X-Ray Diffraction, and Differential Scanning Calorimetry. Polymer Journal. 2006;38(11):1127–1136.

21. Ghosal S, Chen M, Wagner J, Wang Z, Wall S. Environmental Pollution. 2018; 233:1113-1124.

22. Di M, Wang J. Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. Science of the Total Environment. 2018;1620-1627,616-617.

23. Rebollar E, Hernandez M, Ezquerra TA, Garcia-Ruiz JP. Physicochemical modifications accompanying UV laser induced surface structures on poly (ethylene terephthalate) and their effect on adhesion of mesenchymal cells. Physical Chemistry Chemical Physics. 2014;33:16.

24. Andreassen E. "Polypropylene," in Infrared and Raman spectroscopy of polypropylene, Dordrecht, Springer. 1999; 320-328.

25. Guo X, Lin Z, Wang Y, He Z, Wang M, Jin G. In-Line Monitoring the Degradation of Polypropylene under Multiple Extrusions Based on Raman Spectroscopy. Polymers. 2019;11:1698.

26. Khafagy RM. *In situ* FT-raman spectroscopic study of the conformational changes occurring in isotactic polypropylene during its melting and crystallization processes. Journal of Polymer Science Part B: Polymer Physics. 2006;44(15):2173-2182.

27. Michael M, Luca D, Chiara A, Andrew R, Herrington, Simon C, Kishan D. Optimal algorithm for fluorescence suppression of modulated Raman spectroscopy. Optics Express. 2010;18(11):11382.

28. Baibarac M, Stingescu L, Stroe M, Negrila C, Matei E, Cotet LC, Anghel I, Şofran IE, Baia L. Poly (vinyl chloride) spheres coated with graphene oxide sheets: From synthesis to optical properties and their applications as flame-retardant agents. Polymers. 2021;13(4):565.

29. Ludwig V, Ludwig ZMDC, Rodrigues MM, Anjos V, Costa CB, das Dores DRSA, da Silva VR, Soares F. Analysis by Raman and infrared spectroscopy combined with theoretical studies on the identification of plasticizer in PVC films. Vibrational Spectroscopy. 2018;98:134-138.

30. DankO M, Orszagh J, Durian M, Kocišek J, Daxner M, Zottl S, Maljkovic´ JB, Fedor J, Scheier P, Denifl S, Matej S. Electron impact excitation of methane: determination of appearance energies for dissociation products. Atomic, Molecular and Optical Physics. 2013;46(4):045203.

31. Tran M, Sun Q, Smith BW, Winefordner JD. Determination of C꞉ H꞉ O꞉ N ratios in solid organic compounds by laser-induced plasma spectroscopy. Journal of Analytical Atomic Spectrometry. 2001;16(6):628-632.

32. Hu J, Zuo J, Li J, Zhang Y, Ai X, Zhang J, Gong D, Sun D. Effects of secondary polyethylene microplastic exposure on crucian (*Carassius carassius*) growth, liver damage, and gut microbiome composition. Science of the Total Environment. 2022;802:149736.

33. Lei L, Liu M, Song Y, Lu S, Hu J, Cao C, Xie B, Shi H, He D. Polystyrene (nano)microplastics cause size-dependent neurotoxicity, oxidative damage and other adverse effects in *Caenorhabditis elegans*. Environmental Science: Nano. 2018;5(8): 2009-2020.

34. Shen J, Liang B, Zhang D, Li Y, Tang H, Zhong L, Xu Y. Effects of PET microplastics on the physiology of Drosophila. Chemosphere. 2021;283: 131289.

35. Hwang J, Choi D, Han S, Choi J. Hong J. An assessment of the toxicity of polypropylene microplastics in human derived cells. Science of Total Environment. 2019;684:657-669.