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Laser Induced Spectroscopy (LIBS) Technology and Environmental Risk Index (RI) to Detect Microplastics in Drinking Water in Baghdad, Iraq

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ABSTRACT

Drinking water contamination by microplastic particles is a global concern that is becoming increasingly common due to consumer abuse, and we use laser fractionation spectroscopy to examine what microplastic particles in water packaging can do. Several types of bottled water were sampled at several manufacturing facilities in Baghdad. The presence of the measured micropolymer species in water was immediately classified and detected using a laser production resolution spectrometer as well as signal and plasma scattering spectra, various MP polymers "polyethylene terephthalate, polystyrene, polypropylene, polyethylene, and polyvinyl chloride" are five polymers that were successfully detected in drinking water to validate the ability to identify health risk factors based on potential environmental risk index (RI) and potential environmental risk factors (Tin), the results are calculated to show that risk predicates have evolved over a decade depending on the risk factors. To do. The smallest particle was 20 microns and the largest particle was 63.4 microns. Microplastics were detected in 5 out of 10 samples, PET in 4 samples, PS and PP in 2 samples, and PVC in sample 1, the most common polymer in bottled water is polyethylene. The average C/H ratios of the five samples were PE (1.76), PET (1.21), PS (1.52), PP (1.23), and PVC (0.99), on average, the measured trends of C/H values were [PE greater than PS], [PP greater than PET], and [PVC greater than PET]. According to our results, the integration of LIBS technology provides a fast and efficient way to detect microplastics. It has a high resolution of fine particles, allowing the detection of very small particles associated with various adverse effects on human health. The feasibility study for water bottling was approved, and the WHO water quality criteria were confirmed. As a result, we will undertake a thorough analysis of the best water bottling quality. In this study, the initial LIBS signals of several samples were used to completely detect microplastics. Microplastics in bottled water samples have been detected and quantified using LIBS spectroscopy techniques with Ecological Potential Ecological Risk**.** Analytical technology is used to investigate sources, perform research, and collect relevant data, worldwide reports, and permitted statistics to deliver crucial insights and recommendations.Water samples were obtained from several locations throughout Baghdad. At the source, 2 liters of water were obtained in plastic bottles for each sample, for a total of 10 samples. Each sample is owned by the factories that supplied it.

INTRODUCTION

Since 2018, an increasing number of scientists have examined the notion that tap water is precious with a huge impact on a human and a noun component of our everyday life. Most countries emphasize providing people need clean, safe water. However, in recent times, the usage of bottled drinking water has increased, with global consumption reaching 329.33 billion liters per year on average (Johnson et al. 2020, Almaiman et al. 2021, Dalmau-Soler et al. 2021, Gomiero et al. 2021). Although bottled water is a popular option, it has considerable limitations because it is not as tightly regulated as municipal tap water (Mintenig et al. 2019, Lam et al. 2020, Kirstein et al. 2021). The majority of bottled water manufacturers favor plastic packaging, which is rarely recycled. As a result, plastic packaging winds up in landfills or as debris in seas and lakes, where it degrades into microplastic particles as a result of UV exposure, biofilm formation, mechanical shear, and wave action (Sultan et al. 2018). Microplastics can pollute drinking water and pose major health risks such as cancer if consumed by people (Pivokonsky et al. 2018, Pivokonský et al. 2020, Sarkar et al. 2021).

Microplastics are categorized based on their size or origin. Their size determines whether they are considered as little or huge, the tiniest microplastics are 1m to 1mm in size. Based on their origin, microplastics are classed as secondary or primary. Secondary occurs when macroplastics break down as a result of continual exposure to poor environmental conditions. Microplastics have lately been found in a variety of environments, including soil and human feces; there have been a few researches on the prevalence of plastic materials in drinking water bottling. Several methods have been developed for detecting and measuring microplastics in seas, lakes, and groundwater. NIR, FTIR, SEM-EDS, and photoluminescence are among the techniques used (Kirstein et al. 2021). The FTIR method analyzes the molecular structure of a sample by evaluating its response to infrared light. This procedure is non-destructive, trustworthy, and simple (Pivokonsky et al. 2018). However, Because of particle faults in the reflection mode, the efficiency of this technique is significantly reduced. It is best suited for dry materials and particles larger than 10 m in diameter (Pivokonsk et al. 2020). NIR technology can also identify materials by analyzing the molecular vibrations caused by electromagnetic radiation. This method penetrates deeper and Compared to FTIR, it requires less sample preparation. It is, however, restricted to particles with a diameter greater than 1 mm (Domínguez & Luoma 2020, Kirstein et al. 2021). Photoelectroelectron spectroscopy, a new approach for identifying microplastics, is based on the idea that when optically stimulated materials return to their ground state, they release electromagnetic radiation. This approach has proven its worth by discriminating between plastic and non-plastic materials (Andrade & Rhodes 2012, Sarkar et al. 2021). However, this method is impeded by beam overlap, which makes discriminating between different plastics difficult. (Handbook of the Birds of the World 2018, Sarkar et al. 2021). Due to the drawbacks of present technologies, it is necessary to design a technique that is dependable and has the potential to be used in site investigations (Dudley 2008, Ati et al. 2022). There has been little investigation into the use of LIBs and spectroscopy to identify microplastics. A molecular analysis method based on the inelastic light scattering principle. This approach can assess the chemical material and identify constituent particles (Dudley et al. 2010, Domnguez & Luoma 2020). Because of its significant sensitivity to non-polar functional groups, precision in clarity of ultrafine particles, and little interaction with water, this technique has been widely employed in the level assessment of microplastics (Coetzee et al. 2014, Kirstein et al. 2021). This element's characteristic electromagnetic radiation is emitted as a result of the cooling of the plasma containing the excited ions. Polymers were discovered by measuring the carbon and hydrogen line density ratios (Andrade & Rhodes 2012, Coetzer et al. 2014, WHO 2018). Polymers were discovered by studying molecular data. As a result, the study's purpose was to detect microplastics in bottled water samples while also closing a knowledge gap about them from multiple sources. The United States Environmental Protection Agency (USEPA 2006) defines the potential for adverse effects on ecosystems as a result of exposure to an environmental stressor or a combination of environmental factors, and an environmental potential factor is any physical, chemical, environmental stress factors that may have negative effects on certain natural resources, as well as the environment in which they interact with them. The term "risk assessment" refers to describing the nature, magnitude, or amount of health risks to the population as a result of microplastic or any other type of environmental stress that may be present in the environment (Chen 2020). Where it is calculated potential environmental risk index (RI) is calculated by the equation:

$$RI = Tin\ x\ \ CRM / Cio$$

Tin = the concentration of the metal in the sample

Cio = level of pollution value of the metal

CRM= Certificate references materials

To assess concentration, the degree of contamination, pollution ($Cio < 1$), low level of pollution ($1\ Cio < 2$), moderate level of pollution ($2 \leq Cio < 3$), strong level of pollution ($3\ Cio < 5$) and very strong level of pollution (Cio) (EC (2020).

MATERIALS AND METHODS

The liters of water bottled in plastic were gathered from a local vendor for each sample, for a total of ten packaging source samples. LIBS measurements were performed using the method indicated in (Ruas et al. 2017), allowing for direct investigation of water samples for microplastic detection to take accurate volumetric measurements, a glass beaker

Table 1: Factors and degrees of the QA and QC of potential ecological risk factors (Kicińska & Wikar 2023).

Epr value	Grades of ecological risk of metals
Epri< 10	Low risk
10 ≤ Epri < 20 R	Moderate risk
20 ≤ Epri < 30 R	Considerable risk
30 ≤ Epri< 40	High risk
40 ≤ Epri	Very high risk

deionized with water was employed. 100 cc of each collected water sample was placed in a glass holder and then the laser was focused directly to obtain the spectra. The components of the water samples were analyzed using laser-induced breakdown spectrometry to detect microplastics (LIBS). An Ocean Optics LIBS spectrometer was used in this study. Ocean Optics' LIBS2500plus spectrometer equipment was employed. Set the laser power to 300 mJ, pulse width to 10 ns, and PRF to 1-2 Hz. He reached a peak output of 32.25 MW in a second and a half. This device is capable of doing qualitative measurements in real time. Spectra were scanned with a resolution of 0.1 nm (FWHM) between wavelengths 200 and 980 nm. Seven spectral channels with wavelengths ranging from 198.16 to 971.11 nm were incorporated into the system. Ocean Optics provided LIB Splus version 4.5.0.7 for evaluating findings. The software enabled the LIBS 2500plus system to function by detecting different elements' emission lines, correlating background signals, showing emission spectra, collecting data, giving the spectrum, and firing the laser, also includes a spectrum library of 2,500 "National Institute of Standards and Technology" atomic emission lines. The LIBS2500Plus system was detected and calibrated using the emission lines. Each sample was randomly assigned 200 spectrums and evaluated independently, the method was done four times for each of the ten samples to ensure

Determination of the potential environmental risk index (RI) for samples: This was accomplished by determining the CRM (Certificate reference materials) and comparing the measurement results to the certified value reference materials.

CRM of water [(0.91 ± 0.01), (0.01 ± 0.01), (0.81 ± 0.12)]

@Certified value ± 95% confidence interval of the mean value

c Mean ± standard deviation at 95% confidence limit with replicate

Then apply the equation below: depending the Table (1).

RI = Tin x CRM / Cio

Various statistical coefficients of determination metrics, the correlation coefficient of concordance and the correlation coefficient of interclass were used in the analysis of variance, mean prediction of concentration is compared with data from their label and proposed guidelines published by WHO (2012) and USEPA (2009) under the Principal components with the test for significance between individual groups The smallest significant difference in probability at a 5% level (RI). Correlation analysis was also performed to determine the relationship between the heating value and each of the chemical components, as well as the final and proximal analysis, and by using the SAS statistical package to measure properties (Cox 2016).

RESULTS AND DISCUSSION

The atomic spectra generated from the LIBS measurements were estimated based on the vibration spectra obtained from the tests to detect MP in the water samples used in the experiment, which have been identified as commonly used polymers in bottled water packaging. The bands are observed at 1163 cm^{-1} and 1199 cm^{-1}, which are related to C-C bond stretching, 1179 cm^{-1}, which is related to CH_2 rocking vibration, and 1391 cm^{-1}, which are related to CH_2 swing vibration and the CH_2 stretching in Fig 1. The atomic spectra of four distinct materials were calculated using LIBS. On average, The C/H ratio for the five samples was 1.49, the larger C/H value is related to it (WHO 2018, Ajmi et al. 2018), which also suggests the presence of polyethylene.

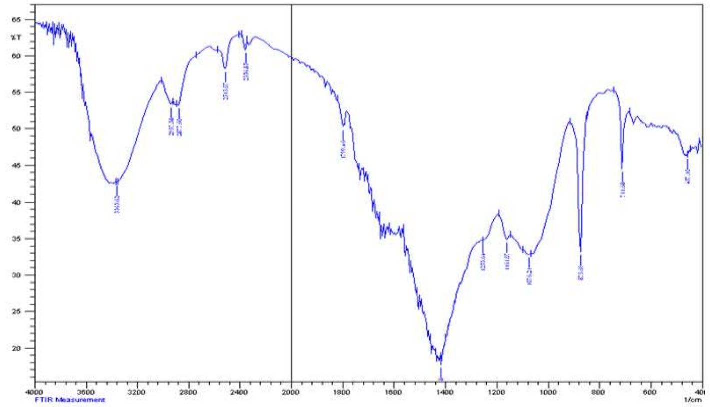

Fig. 1: LIBS spectra for samples containing polyethylene.

At 898 cm^{-1}, It also showed asymmetric stretch vibrations for both C-C and C-(O)-O bonds, while symmetric stretch vibrations were detected for C-O-C bonds, which bind to 1138 Cm-O-C and Cm-O, are detected at 1096 cm^{-1}, 1285 cm^{-1} of C-C bond stretching vibrations, 1395 cm^{-1} of C(O)-O bond stretching vibrations, 1430 cm^{-1} of O-CH, CH2, and C-CH bond bending vibrations, and 1645 cm^{-1} of 8a Circular mode vibrations = 1730 in the Wilson extension (Fig. 2). The four samples' average C/H ratio was 1.11, which is comparable to been reported by (WHO 2013, Ruas et al. 2017), It provides evidence for the existence of polyethylene terephthalate in the sample.

The readings indicated two of the 10 samples had ranges of 388 cm^{-1} due to CH bending and CH_2 bond shaking, 899 cm^{-1} due to vibrations between CH, C-C and C-CH_3 bonds, and 893 cm^{-1} due to vibrations between CH bonds (Fig. 3). And CH_3 and C, which leads to the curvature of the C-CH_3 and C-C bonds of 1140 cm^{-1}. Torsion of CH_2 at 1330 and 1488 cm^{-1} caused bending vibrations of CH, CH_3, and CH_2. The two samples' average C/H ratio was 1.27. The methyl and methylene groups in PP repeat units make them up. The obtained ratio is significantly different from the measured by (WHO 2013, Kukkala & Moilanen 2013), which are polypropylene-based.

Ring deformation was identified in two more samples out of ten, including a notable peak at 1001 cm^{-1} due to the aromatic carbon ring's circular breathing mode, a band of 1031 cm^{-1} due to CH in-plane deformation, and 1155 cm^{-1} due to 1451 C_2 stretching vibrations. Vibrations of structural rings are stretched and agreed with WHO (2013), Kukkala & Moilanen (2013), Coetzer et al. The visible bands are shown in Fig. 4.

PS bands of 361 cm^{-1} were detected in one of the water samples due to the brief formation of a The C-Cl bond was in the PVC polymer, 618 cm^{-1} concussions for the C-Cl stretch, and 1485 cm^{-1} for the C-H homolog in the CM group. The band image is depicted in Fig. 4. These are PVC-specific peaks (WHO 2013). PVC has many additives which represents a sample mean C/H of 0.95. According to the value calculated by (Dudley 2008, WHO 2018, Fadhel 2019).

LIBS experiments detected atomic spectra lines at several characteristic wavelengths when the intensities of

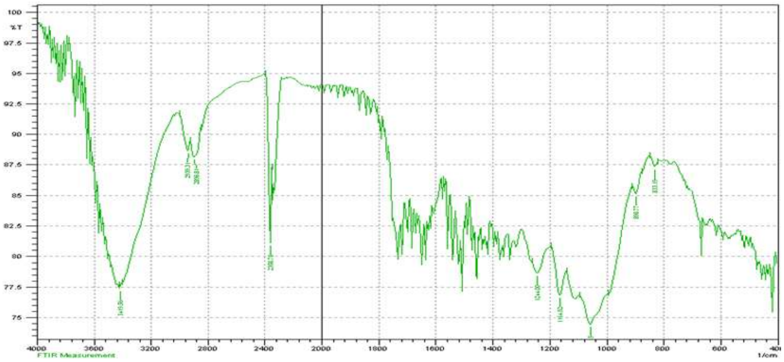

Fig. 2: PET-containing materials' LIBS spectrum.

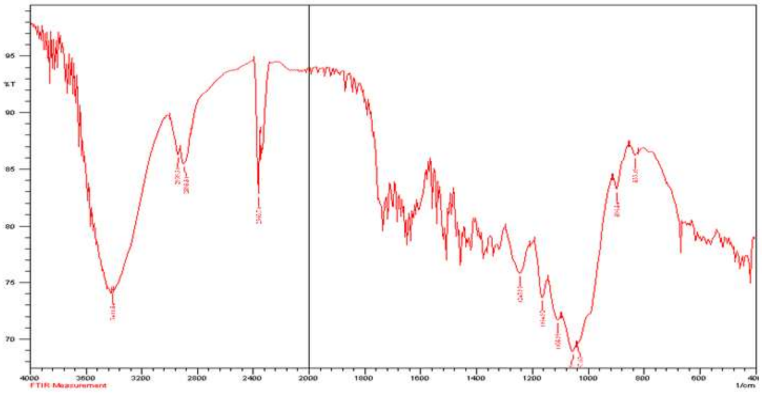

Fig. 3: LIBS spectra for samples containing PP.

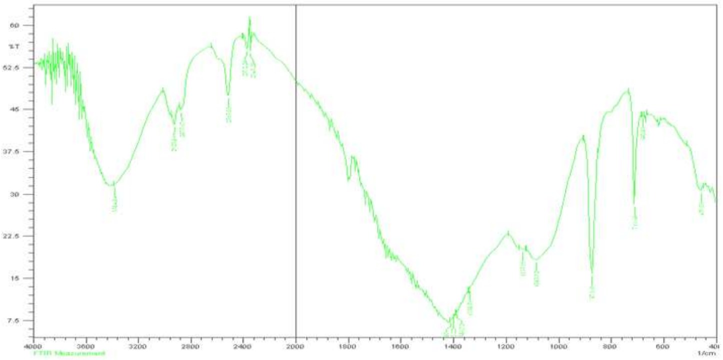

Fig. 4: LIBS spectra for samples containing PS.

specific spectral lines were drastically increased, when the interference from the emission lines is reduced, it leads to less absorption of particles. The transmission line at 257.81 corresponds to the electrical transition from the 2s22p2 to the 2s22p3s state in the LIBS observations. Hydrogen atoms make up emission line 398. The atomic of emission line 656.3 is the source of H atoms transitioning from energy levels in level 3 to lower energy levels in level 2. At 725.7 nm, PVC is the sole material having a noticeable Cl line (Dudley et al. 2010). An O(I) atom migrating from 2s22p33s to 2s22p33p triggers the 777.3 emission line, indicating LIBS's ability to detect trace elements.

To confirm the capacity to identify the elements in health risks according to the Potential Ecological Risk Index (RI) and potential ecological risk factor (Tin) in dynamic modeling to predict changes in water concentration in environmental compartments exposure by calculating the concentration of microplastic and its concentration in the reference value

$$RI = Tin \times CRM / Cio$$

Tin = Concentration of metals in the sample Cio = reference depending Table (1)

CRM Certificate Reference material in metal

The prediction for more than or less than ten years depends on Exposure Factors.

Results in water in five samples [1.00**, 0.82**, 0.02, 0.51*, 0.05]

* Average values to predicate risk for more than < ten years depending on Exposure Factors accumulated

** Average high values to predicate risk less than > ten years depending on Exposure Factors accumulated

The results showed that the percentage of pollution as indicated is more vulnerable to pollution in the coming years. The results of the Potential Ecological Risk Index of concentration that have been obtained from analyzed samples were reached of the bioindication environment and how to transition microplastic to water, according to Sultan et al. (2018) and Cristol et al. (2008).

CONCLUSIONS AND RECOMMENDATIONS

This study was successful in identifying microplastics in plastic drinking water, with The tiniest particles measuring 20 m, while the largest measured 63.4 m. Microplastics were discovered in five of 10 samples, PET in four, PS and PP in two, and PVC in one. According to the study's findings, polyethylene is the most frequent polymer in bottled drinking water; the average C/H ratios of the five samples were PE (1.76), PET (1.21), PS (1.52), PP (1.23), and PVC (0.99). On average, the measured trend for C/H value was [PE more than PS], [PP greater than PET], and [PVC greater than PET]. Polymers were present in the water samples, based on the ratios. According to the findings, integrating LIBS technologies gives a quick and efficient technique for detecting microplastics. It has a high microscopic particle resolution and so can detect very minute particles. The approaches are also non-polar functional group sensitive and are unaffected by water samples. This study will help to direct future detection and classification research. Microplastics have also been linked to a variety of negative health impacts in humans. Identify and learn about critical actions for lowering their health consequences. As a result, the techniques investigated in this study can be utilized to detect and quantify in industrial environments. Its use will assure the availability of healthy drinking water that is free of health concerns.

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