Initiating the development of a library for plastic polymers using Raman spectroscopy

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1. Abstract

Plastics, and particularly microplastics (MPs, plastic pieces <5mm), are ubiquitous and have developed into a serious issue for our marine environments. Not only do they pose a threat to aquatic organisms directly exposed to plastic pollution, but there is also a potential risk to humans further down the line, due to prolonged exposure to these small particles through the food they eat, the air they breathe, or the water they drink. Scientific evidences have been provided showing that plastic polymers have been detected in human blood, as well as in the placenta or human stool. Consequently, it is critical to assess the sources of MPs exposure to humans. One source is table salt, particularly when it comes from sea salt. The characterisation and detection of such small particles remain an analytical challenge due to their small size, the quantity of material available, the colour of the material, and the natural organic matter that can adsorb onto MPs degraded in the environment. Raman spectroscopy is one of the leading tools for MPs analysis as it is non-destructive and requires little to no sample preparation with a spatial resolution of 1 μm. However, in order to identify these tiny pieces of plastic, reference spectra are needed. There are many obstacles in providing these spectra that make building up a library challenging. This project set out to not only initiate the process of creating a plastic polymer library using Raman spectroscopy, but also to identify potential interferences. 15 different samples of plastic litter were analysed and added to the library, and possible challenges were identified. The project provided a foundation for further research and development.

2. Aims

The overall aim of the project was to begin developing a plastic polymer library using Raman spectroscopy on known plastic litter samples. This library aims to provide a more comprehensive characterisation than existing commercial libraries, thereby enhancing confidence in the material characterisation of environmental samples.

Specific objectives:

1) Collect plastic litter samples.
2) Analyse the samples using Raman spectroscopy.
3) Identify potential interferences in Raman spectroscopy, such as complications with dyes and fluorescence.

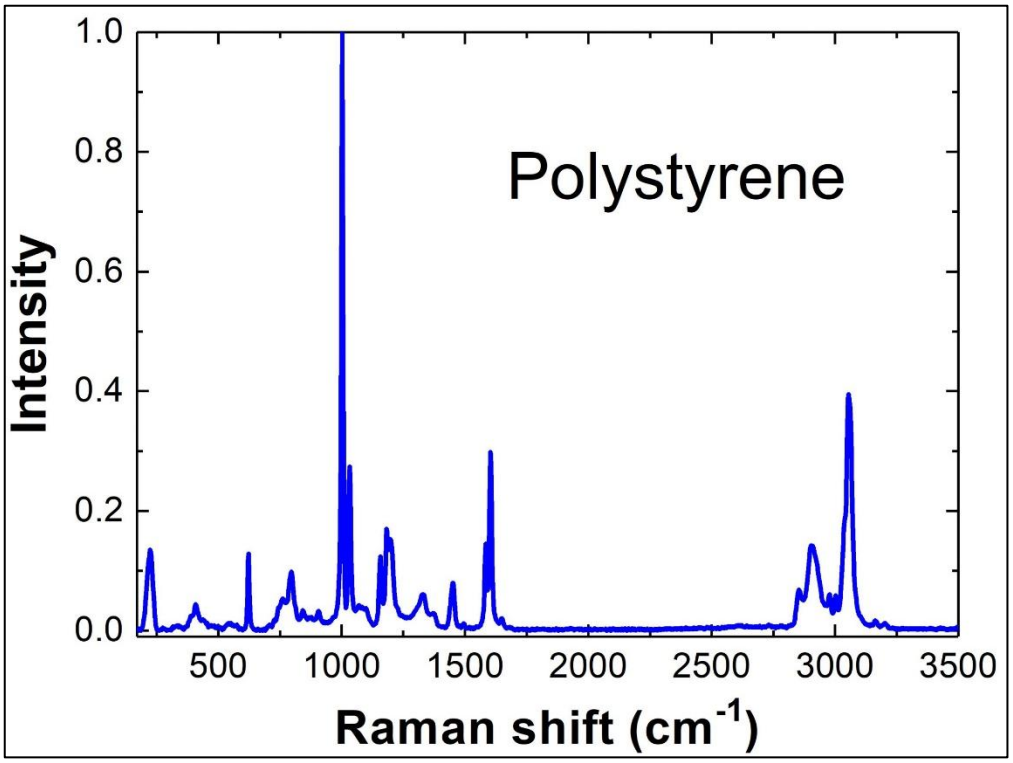
3. Introduction

Plastic, due to its versatility and functionality, is used in a range of different circumstances including many single-use items such as packaging. A poor recycling system for plastic polymers has resulted in plastic accumulating in the environment.[1] Despite most plastic waste going into landfill where it remains for many hundreds of years due to its long decomposition time [2], some waste ends up in the aquatic environment, with an estimate in 2019 saying that around 171 trillion plastic particles, primarily microplastics (MPs, plastic particles <5mm in size), are floating in the sea.[3] MPs can be categorised into two sources: primary MPs, which are particles manufactured to be a microscopic size, and secondary MPs, which form from the breakdown of larger pieces of plastic on land and at sea through weathering.[4] The buildup of these MPs in aquatic environments has a negative impact as it is a direct threat to the marine food chain.[19] It not only decreases the lifespan of organisms impacted (usually through eating MPs or by eating smaller organisms that have) but also poses a human risk as the levels of toxicity might build up through the trophic levels.[5]

Detecting and characterising MPs in environmental samples represents an analytical challenge. MPs are problematic to analyse mainly due to their small size (<5mm), and there are intrinsic difficulties in collecting, handling, identifying and characterising MPs from environmental samples.[6] The two most popular analytical tools used for identifying these MPs at the moment are Raman spectroscopy and FT-IR (Fourier Transform - Infra-Red) spectroscopy.[7] In this instance, there is an advantage for using Raman spectroscopy as Raman has a spatial resolution of 1µm which is much better for MP analysis than the 100µm spatial resolution of FT-IR. The measurements of both FT-IR and Raman are complementary as Raman spectroscopy allows better identification of non-polar, symmetric bonds whereas FT-IR gives clearer signals of polar groups.[16] Raman spectroscopy is ideal for MP analysis as it is generally non-destructive and requires little to no preparation of the sample.[18] Due to its small spatial resolution of 1 µm it has the capacity to analyse a wide range of MP sizes, i.e. above 1 µm. [20] Raman spectroscopy is an increasingly popular analytical tool used for a range of disciplines from chemistry [8] to medicine[9] to geology.[10]

Raman spectroscopy works by measuring the shift in frequency of inelastically scattered light which it creates by firing photons at the sample using an excitation source, i.e. a

laser. Scattered light is made up of two parts: elastic scattering and inelastic scattering. Elastic scattering has the same wavelength and frequency as the photons from the laser and is much more common whereas inelastic scattering, which only happens to one out of every 10^7 photons[11], changes frequency which is then measured in order to work out the molecular structure of the sample. This scattered light is produced by a photon from the laser hitting a molecule of the sample which emits a scattered photon. If the scattered photon has a lower frequency than the photon from the laser then this is called Stokes Raman scattering and if it has a higher frequency, it is named anti-Stokes Raman scattering.[11] Different shifts are characteristic of certain functional groups, allowing us to piece together the structure of the molecule from its Raman "fingerprint" (see Fig. 1 for an example).



Anon, (n.d.). *Polystyrene Raman spectrum | Raman for life*. [online] Available at: https://ramanlife.com/library/polystyrene-raman/.

Fig. 1

Fig. 1 shows the Raman spectrum of polystyrene. We can reconstruct the shape of the molecule by looking at the Raman shift of the peaks, so, for example, the large peak at ~ 1150 cm^{-1} corresponds to a C-C stretch and the peak at ~ 1450cm^{-1} corresponds to CH_2 scissoring (a certain type of bending vibration of CH_2 groups).

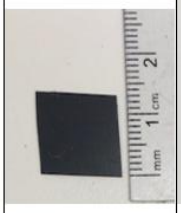
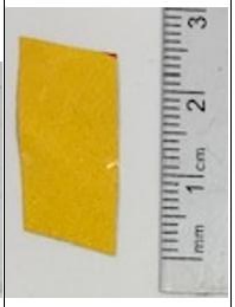
4. Method

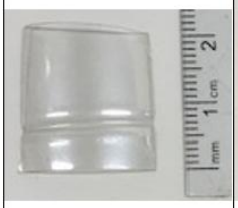
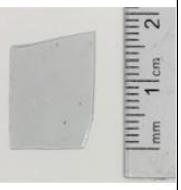
Sample collection.

Initially 15 samples were collected from commonplace plastic items (mainly food packaging). These samples were prepared by cutting them into small pieces varying in size from 1cm to 3cm using scissors. The aim was to provide at least three pieces per

sample where possible, as there was a risk of samples being burned by the laser during Raman spectroscopy if due care was not taken. These samples were sorted into 15 labelled plastic pots and handled using tweezers to minimise interference with the spectra that might have been caused by human touch. The samples were placed onto a glass microscopic slide, with non-flat samples being weighed down on both sides by smaller glass slides.

- ***Interference Investigation***
  In order to investigate the effects of different dyes on the same plastic, five samples were cut from the wrapper on the outside of a Pepsi bottle (see table below), one for each of the five colours used in the wrapper. Despite all coming from the same wrapper, there were many differences between the spectra which will be described in depth later (see 7. Pepsi Wrapper comparison).

Sample name	Photo of sample	Parameters used when taking Raman spectrum
Black Coffee Lid		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x5
Black Film from Chicken Bites		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x3
Cap of Gas Cylinder		Excitation: 785nm Laser power: 0.2mW Exposure time: 60s Spectra Collected: x3
Chicken Bites Box		Excitation: 785nm Laser power: 1mW Exposure time: 45s Spectra Collected: x5
Clear Film from Chicken Bites		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x5
Marylands Wrapper – Red		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x3
Marylands Wrapper – Yellow		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x3

Cherry Pepsi Bottle		Excitation: 785nm Laser power: 0.2mW Exposure time: 30s Spectra Collected: x3
Cherry Pepsi Cap		Excitation: 785nm Laser power: 0.5mW Exposure time:45s Spectra Collected: x3
Cherry Pepsi Wrapper – Black		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x5
Cherry Pepsi Wrapper – Blue		Excitation: 785nm Laser power: 0.5mW Exposure time: 60s Spectra Collected: x5
Cherry Pepsi Wrapper – Green		Excitation: 785nm Laser power: 0.5mW Exposure time: 60s Spectra Collected: x5
Cherry Pepsi Wrapper – Red		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x5
Cherry Pepsi Wrapper – White		Excitation: 785nm Laser power: 1mW Exposure time: 60s Spectra Collected: x5
Tomato Box		Excitation: 785nm Laser power: 1mW Exposure time: 45s Spectra Collected: x5

The above tables contain the names of all 15 samples, with a photograph of the samples next to a ruler, and finally the parameters used when producing their Raman spectrum.

The work was completed using the Raman microscope (see Fig. 2). The prepared slide was inserted into the instrument onto the bed, which was further moved using the joystick so that the sample was directly under the beam of light. Then the doors were shut, and the microscope was focused using the wheels under the bed to get it close and the wheel on the side of the joystick was used to adjust it. A picture was taken of the sample under the microscope in order to compare any visible similarities at a later date.

Fig. 2

The instrument used; a Thermo Scientific™ DXR3 Raman Microscope equipped with a 785nm excitation laser source.

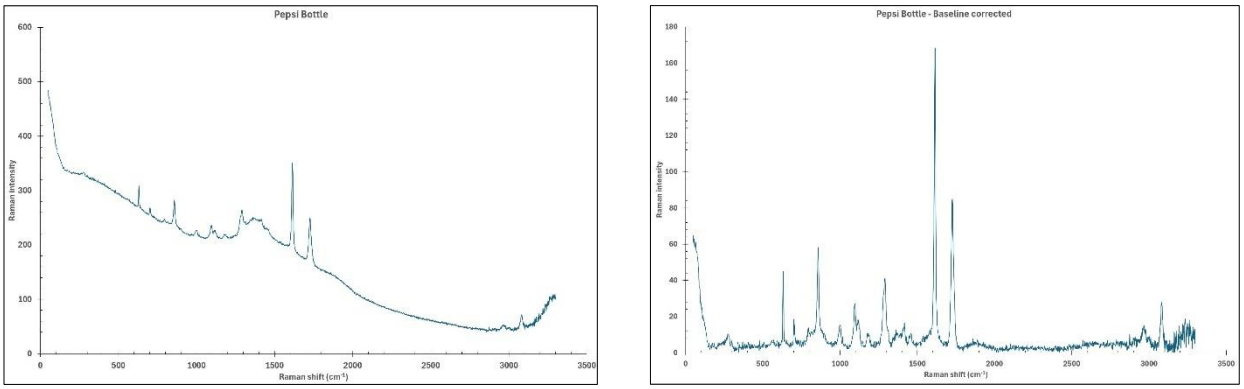
Initial steps of optimisation. The first step once the sample was ready was to run a quick test to produce rough initial spectra. Turning off the lights in the lab was essential in order to reduce the level of interference with the spectra caused by exterior photons entering the instrument (see 6.5 Light Interference). Running the initial spectrum was useful to enable changes to the laser power in real time, allowing us to see whether the sample will produce a weak or strong spectrum, and also to test what laser power the sample can withstand for an extended period of time. The camera showing the microscope's image of the sample shut off when the laser was on so the next step was to check that the sample had not been burned by the laser, although this did not happen at all. If the sample showed strong peaks when using 1mW excitation (laser power), the laser power was turned down to 0.5mW to see whether the peaks were just as strong, as having a high excitation, whilst increasing the strength of the peak, also lowers the wavenumbers of the peaks, allowing them to bunch up more and become less distinct.

Exposure time. The exposure time was the time taken to run one spectrum and increasing exposure time increases the strength of the peaks. Generally, 60secs exposure time was used, however for some samples with very strong results, 45secs or even 30secs exposure time were sufficient.

Spectra. The final parameter modified was the number of times spectra were taken, with the minimum for the instrument being two as it takes an average between the two, eliminating false peaks that originate from cosmic rays and other interference (see section 6. Issues with identification). Mostly five spectra were taken per sample with a few exceptions for which only three spectra were obtained. The laser wavelength of the instrument used was 785nm.

Background correction. After the spectra had been taken and the final spectrum had been produced, a few issues needed to be dealt with in order to create the best spectrum for that sample. In order to counteract the interference caused by fluorescence, we added a fluorescence filter through the instrument's software to the spectrum which removed the hump in the baseline (see Fig. 3). The fluorescence filter subtracts the background by taking advantage of the fact that the curvature of the baseline is much less sharp than that of the Raman peaks.

Almost all spectrum still needed some manual baseline correction as the baseline (see Fig. 3) was not level. A spline tool was used to select points along the actual baseline in order to give the final spectrum a straight baseline. This was essential when dealing with the data as clear spectra are needed when it comes to future use for MP identification.



A **B**

Fig. 3

Graph A shows the spectrum of a sample taken from a Pepsi Bottle before baseline correction – the curved baseline shape is due to fluorescence. Graph B demonstrates the same spectrum but after using baseline correction techniques. The techniques used for this spectrum were applying a fluorescence filter and manually correcting the baseline using a spline tool (see above for details).

5. Analysis of results

After each spectrum had been taken and corrected, the next step was to analyse the spectra against the known database stored on the computer. This system compares the spectrum provided against the commercial database using both the Raman shift, also

known as the wavenumbers (on the x-axis), of peaks (measured in cm^{-1}) and the relative intensity of the peaks (on the y-axis). This information was entered into a report with the 10-15 best matches that the spectrum had with the database. Although some samples had excellent matches in the 90th percentile, others were not as straightforward with the closest matches being as low as 32%.

The reason these spectra have been taken is to initiate the creation of a Raman spectra library for plastic polymers. In order for the spectra to be ready for entry into the library, the peaks must be labelled precisely on each spectrum to ensure that matching MP samples in the future is as easy as possible, and to allow for the identification of the molecular structure of the sample. Therefore, for every sample a graph was created with each peak being labelled with its Raman shift (in cm^{-1}) (see Fig. 4).

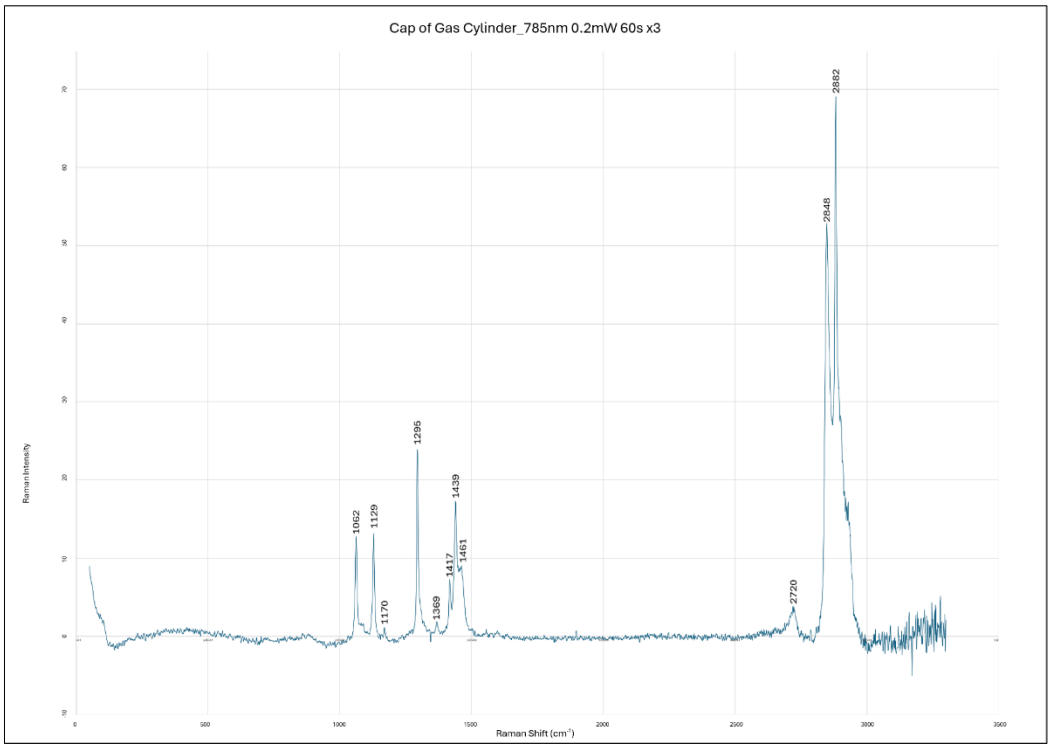


Fig. 4

Example of spectrum with labelled peaks

After labelling the peaks on every spectrum, a table was created for each sample with all of the peaks next to the possible bonds creating that peak. This helps to build up more information about the sample on top of the analysis provided by the database on the computer, as it can provide an explanation for smaller peaks that do not feature in the top match. For all labelled peak tables see section 12. Data.

6. Issues with identification

There are a range of complications and hurdles to overcome with Raman spectroscopy and plastic identification.

6.1 Dyes

Dyes, along with other additives to plastic such as pigments, can have a significant effect on the ability to recognise the spectrum of the sample.[12] This is because the dyes emit fluorescence, which has a large impact on the appearance of the provided spectrum, obscuring the peaks on the spectrum from the sample.

To investigate the impact of different dyes on the spectra of samples from the same plastic, a small investigation was conducted using five samples from a Pepsi Bottle wrapper – each one being a different colour (see 7. Pepsi Wrapper Comparison for results).

6.2 Fluorescence

Fluorescence is caused by the absorption of light by a molecule, which excites the molecule to a higher electronic state. The molecule drops back down to its ground energy state by vibrational relaxation and the emission of a photon with a lower energy than the initial photon, meaning it has a higher wavelength and a lower frequency. If the sample produces even a weak amount of fluorescence in the spectral range (the range of wavenumbers measured for Raman spectroscopy), the Raman scattering can be interfered by the signals produced, meaning fluorescence is known as the Raman Achilles' heel.[13]

785nm is a near-IR (or NIR) wavelength that is a very popular excitation source for Raman spectroscopy as it minimises the effect of fluorescence whilst also providing strong Raman peaks.[14] This is because the energy of the excitation source is not enough to excite the molecule to the higher electronic state.[15]

6.3 Photobleaching

Photobleaching is one way to counteract the effects of fluorescent molecules in the sample by exposing it to radiation from the excitation source for an extended period of time. Whilst we did not intentionally use this technique as a counter to fluorescence, as we were exposing the sample to the laser whilst running the test spectrum, the computer system warned us that the spectrum showed signs of photobleaching which would have probably minimised fluorescence (as none of the samples showed any sign of burning or extreme degradation after the test spectrum).

6.4 Cosmic Rays

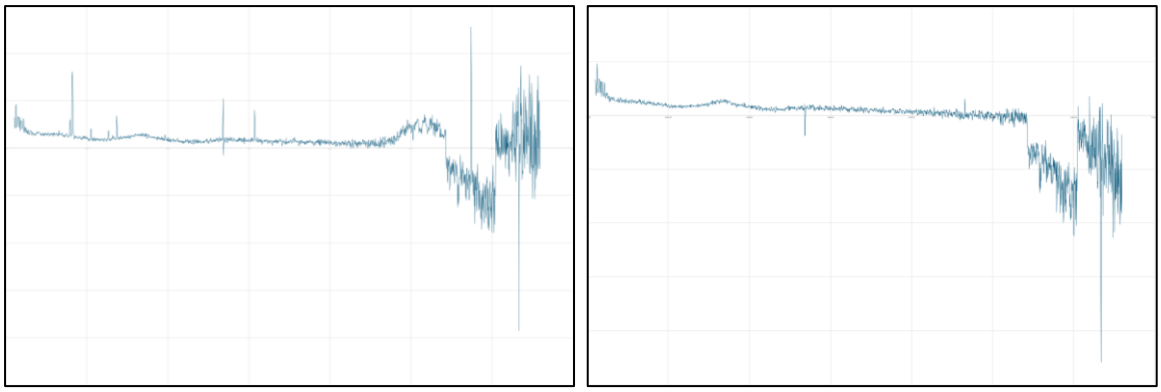
Cosmic rays (high energy charged particles) can cause random giant peaks on the spectra which can dwarf the signals from the sample. These are easy to spot as they create very sharp peaks on the spectrum. They have no influence on the final spectrum provided as they disappear once the second exposure has ended and the anomaly has been taken out. This is due to cosmic rays random nature in time and space, meaning

that as long as you run two exposures (which is the minimum anyway), you can easily overcome this obstacle.

6.5 Light interference

Another factor that could have had a large impact on the spectra was light interference from the ceiling lights in the lab. Photons from the lights were finding their way into the instrument whilst the spectrum was being taken and creating false peaks which decreased our ability to match the spectrum in the future effectively.

In order to illustrate this, a spectrum was taken with the lights on and with no laser power, meaning that any peaks provided were from the lights, and a spectrum was then taken with the lights off and no laser power (see Fig. 5).



Light on Light off

Fig. 5

As is clearly visible, the light being switched on caused around seven peaks that would not have been created if the light had been off.

In order to counteract this effect, we conducted all of the tests with the lights off so as not to have any false peaks on our spectra which would cause later problems.

7. Pepsi Wrapper Comparison

The five spectra produced from the different colours of the Pepsi Wrapper were all unique, despite some showing a few similarities between each other. In order to demonstrate the differences between the spectra, all of the data was added to the same graph with five different lines on it (representing the five colours) and the lines were put one above each other in order for similarities and differences to be more clear (see Fig. 6).

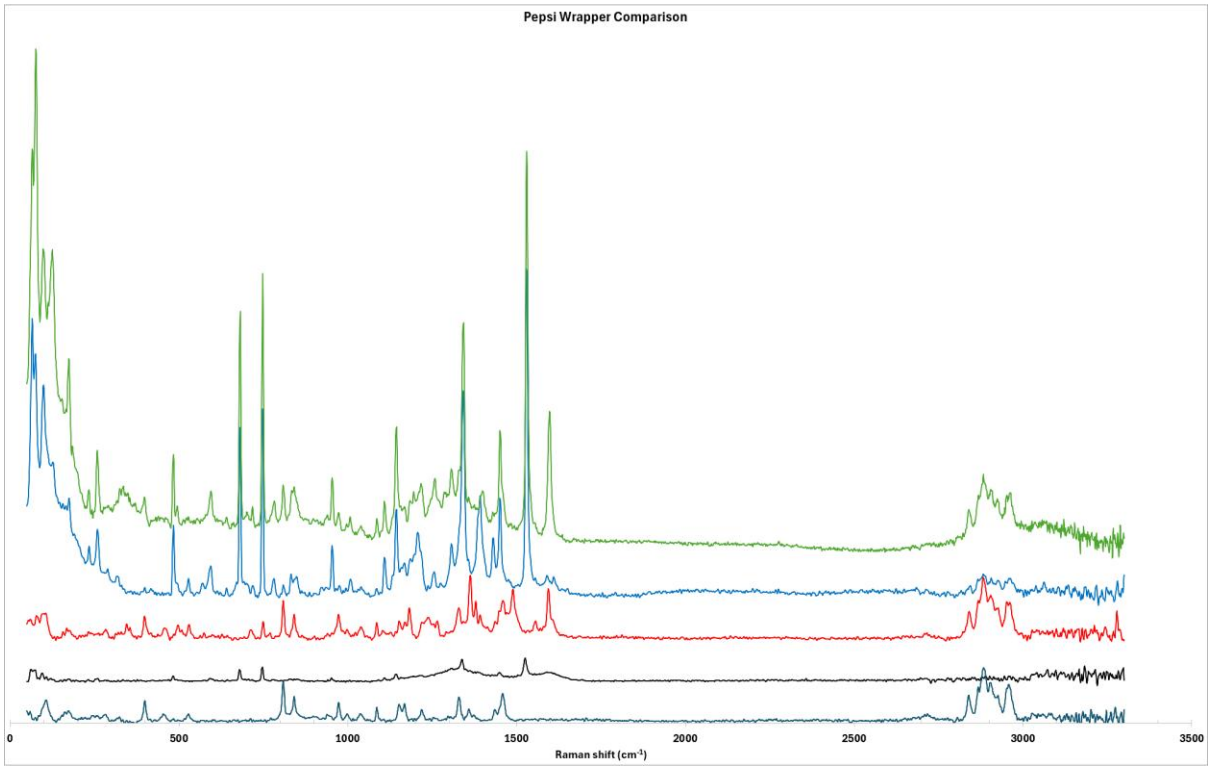


Fig. 6

Fig. 6 shows the spectra of the five different samples taken from a Pepsi Wrapper, which are stacked on top of each other for clearer reading. Only the Raman shift (the x-axis) is relevant here as Raman intensity (y-axis) doesn't help much with compare the peaks.

Although this does show some similarities between the more prominent spectra, blue and green, it doesn't allow for any comparison with the weaker signals such as white or black. In order to make the signals more equal, the y-axis was changed from Raman Intensity (which is very different between colours) to relative intensity (relative to the highest peak on the spectrum).

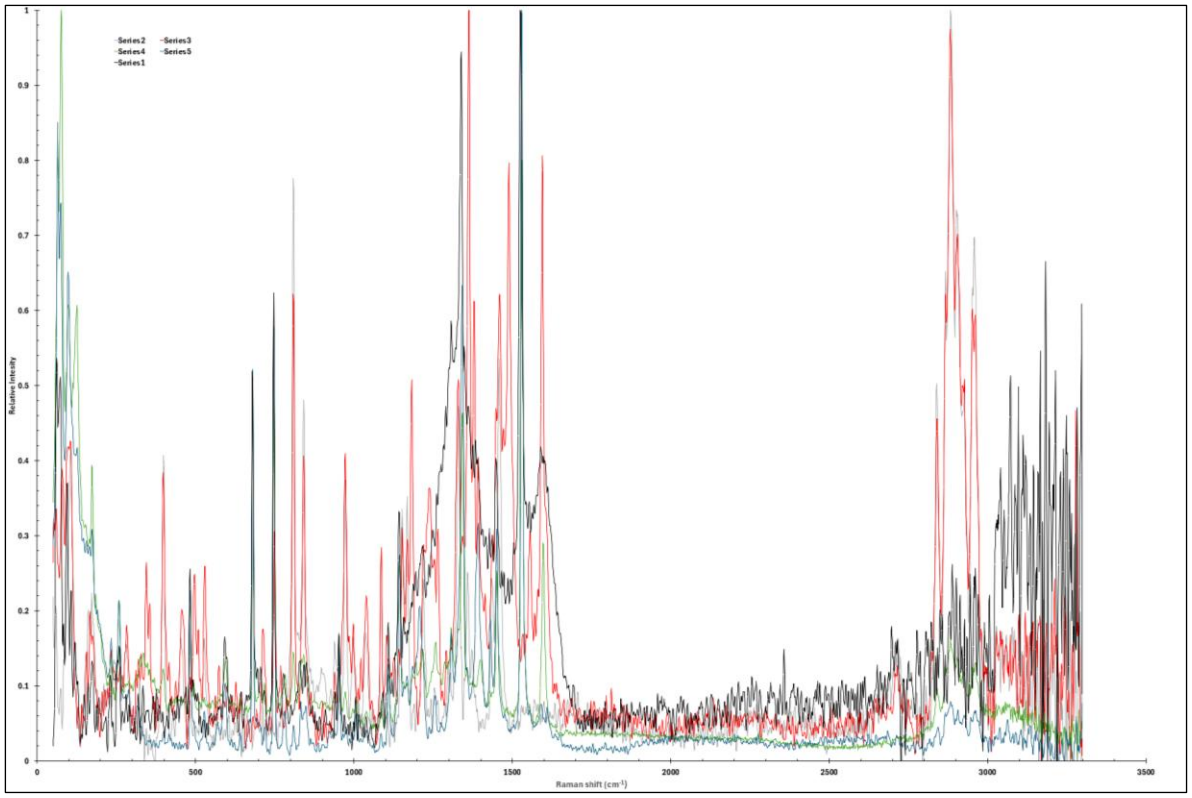


Fig. 7

This graph shows the spectra of the five samples taken from a Pepsi wrapper after having changed the y-axis to relative intensity instead of Raman intensity.

However, this is very noisy due to the lower S/N (signal/noise) of the weaker spectra. In order to compare all of the lines, we looked at the tables produced for the five colours earlier in the analysis of results section (for table see Data section at the end). This made it easier to distinguish common and unique peaks for each spectrum.

Another interesting difference between the five colours were the large differences in Raman intensity (which can be observed in Fig 6). Green gave the strongest signals with a highest intensity of around 125, with blue second with 81. The other three spectra were significantly less intense which could be explained in a few ways.

First of all, we are going to assume that the wrapper is made of one base plastic polymer which is then dyed in order to create the colours.

One possible explanation is that the red, black and white dyes were metal based, which could obscure/dampen the strength of the signals from the plastic behind. Most metals and alloys are Raman inactive due to their electronic structures and symmetry.

The more probable explanation is that the dye/colourant in the red, black and white samples produced fluorescence in the measured range which drowned out the signal from the plastic. It has been reported that the colour of plastic particles can influence the quality of the provided spectra, and that the measurements of red and yellow particles

are usually more affected.[17] Therefore the reason that the spectra were so weak, is because the peaks have been covered up by a much larger amount of fluorescence by comparison to the green and blue samples.

8. Conclusion

In conclusion, the time spent on this project has started the process of building a polymer library. The initial analysis has highlighted a number of issues that will continue to be a challenge as further plastics are added. However, these challenges need to be overcome in order to produce a comprehensive database that can be referred to in the future.

During the course of the project, 15 different plastics were analysed and added to the polymer library. Even with this limited sample size, there were significant challenges with fluorescence and dyes. This highlights the scale of the challenge associated with MP analysis. However, as this project is conducted on a larger scale, it is likely that more plastics with similar properties will be identified.

9. Further possible research

The next steps for this research would be to take the 15 plastic samples and break them down into MP pieces using cryomilling. These MPs could then be examined in order to see any differences in the spectra provided or could be exposed to aquatic conditions and more degradation in order to simulate the effects of MPs within the marine environment for an extended period of time. After this it would be interesting to compare the results provided from Raman spectroscopy in order to understand the effect of these conditions on the molecular composition of the MPs, and to assess the difficulty in identifying these MPs compared to the large plastic litter.

10. Acknowledgements

I would like to thank Dr Maya Al-Sid-Cheikh for all of her help in not only facilitating the project but also for reading through and checking my report. She was extremely generous with her time throughout. I would also like to thank Andrei for patiently supervising me whilst producing the Raman spectra and for highlighting some key interferences with the results.

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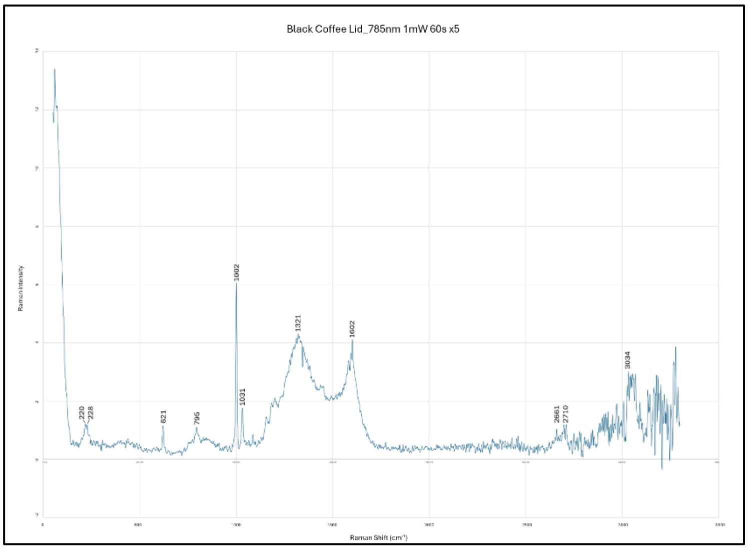
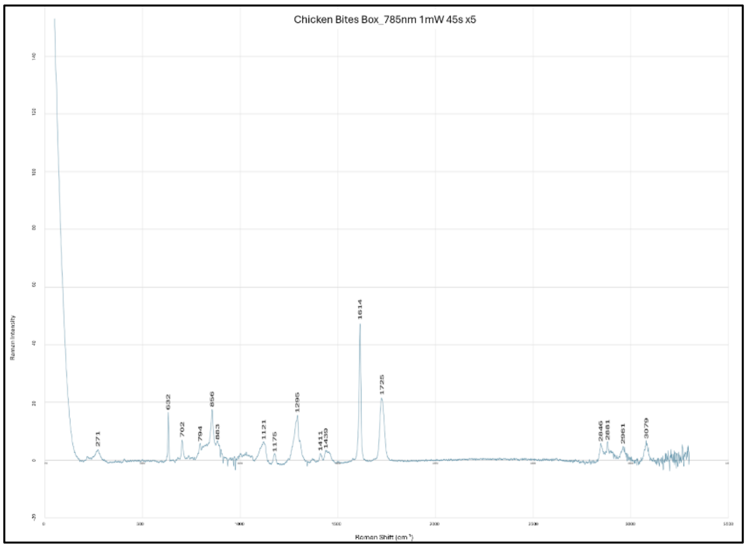
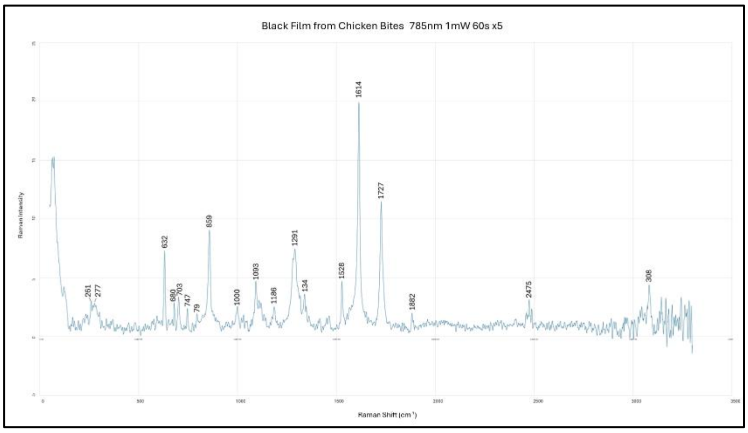
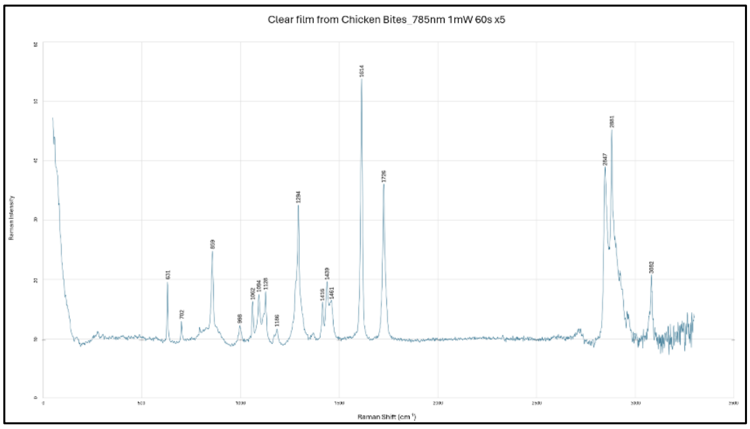
12. Data

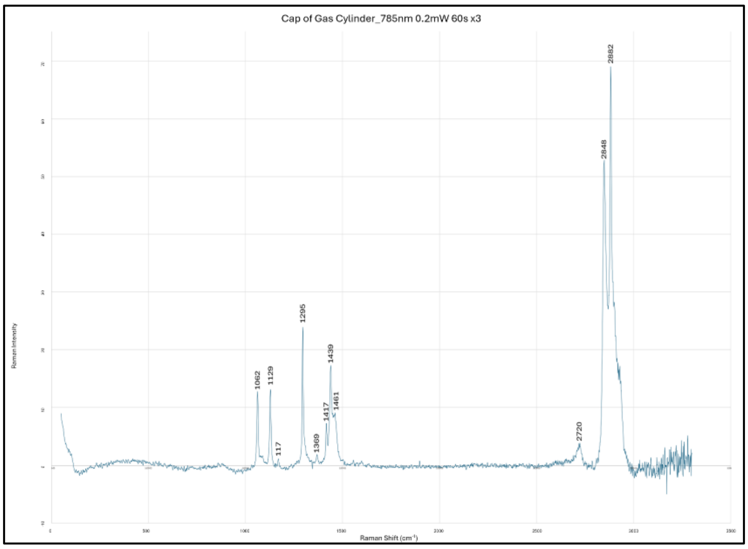
The graphs below show all of the labelled spectra for the fourteen samples tested, with the parameters used in the title of each graph.

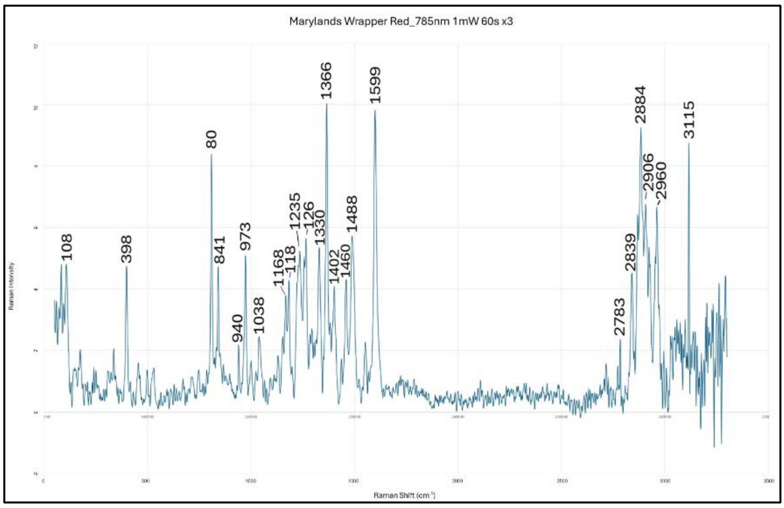

Black Coffee Lid_785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
220
228
621
795
1002
1031
1321
1602
2661
2710
3034

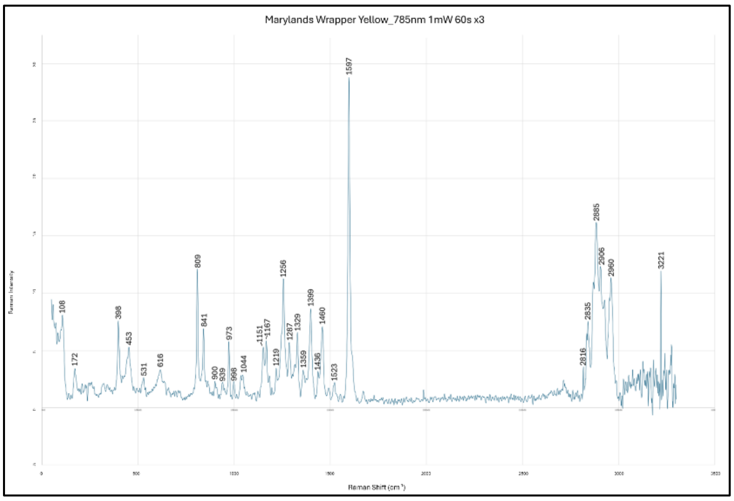

Chicken Bites Box_785nm 1mW 45s x5
Raman Intensity
Raman Shift (cm⁻¹)
271
632
702
794
856
883
1121
1176
1295
1411
1439
1614
1725
2846
2881
2961
3079

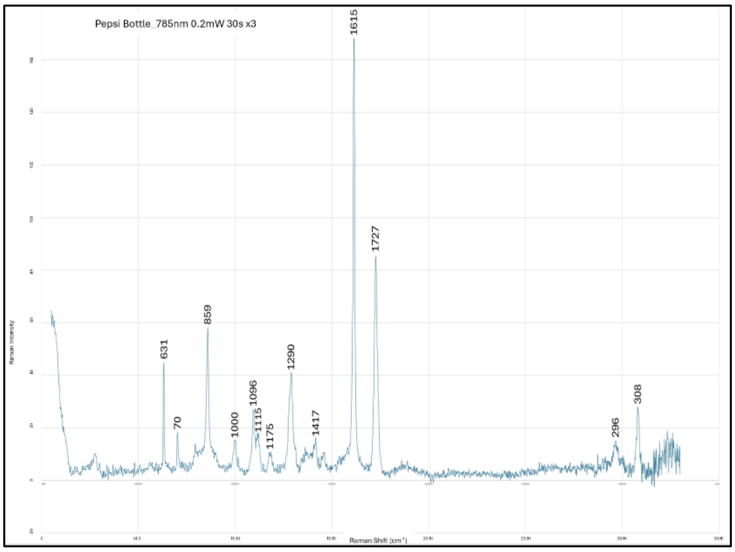

Black Film from Chicken Bites 785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
261
277
632
680
703
747
79
859
1000
1093
1186
1291
134
1528
1614
1727
1882
2475
308

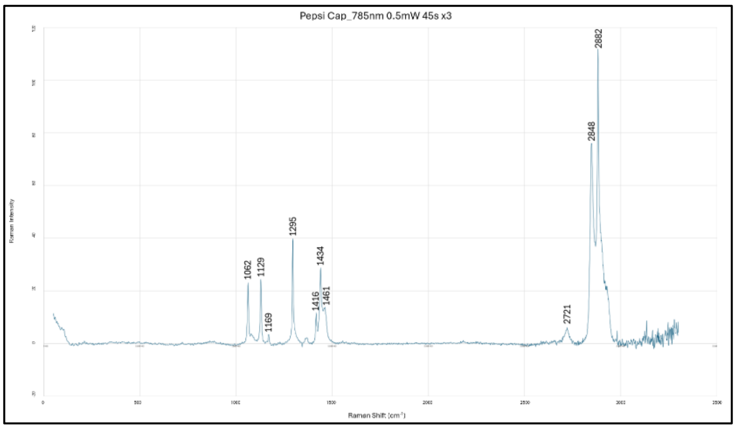

Clear film from Chicken Bites_785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)

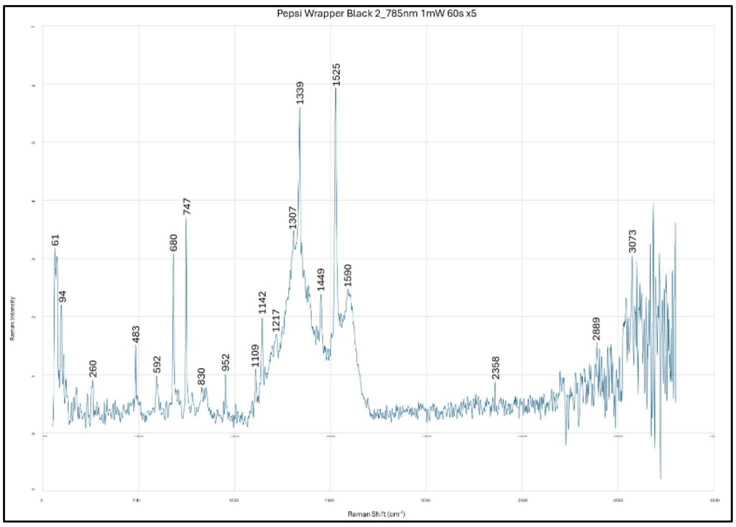

Cap of Gas Cylinder_785nm 0.2mW 60s x3
Raman Intensity
Raman Shift (cm⁻¹)
1062
1129
117
1295
1369
1417
1439
1461
2720
2848
2882

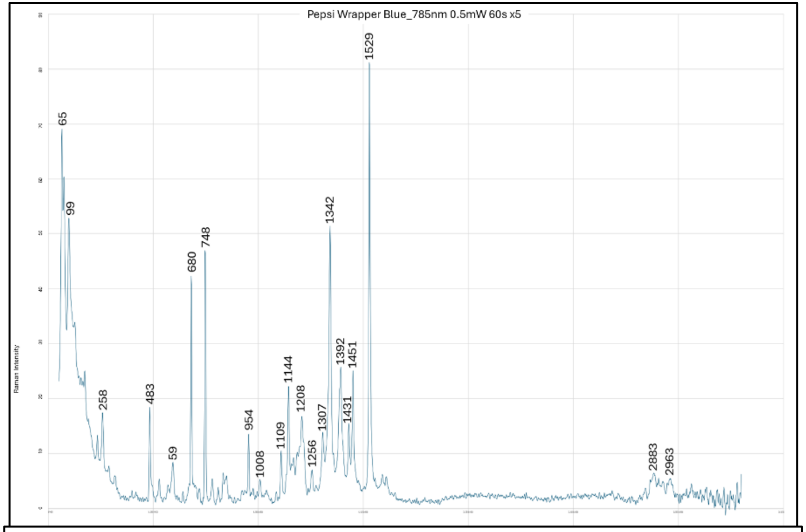

Marylands Wrapper Red_785nm 1mW 60s x3
Raman Intensity
Raman Shift (cm⁻¹)
108
398
80
841
940
973
1038
1168
118
1235
126
1330
1366
1402
1460
1488
1599
2783
2839
2884
2906
2960
3115

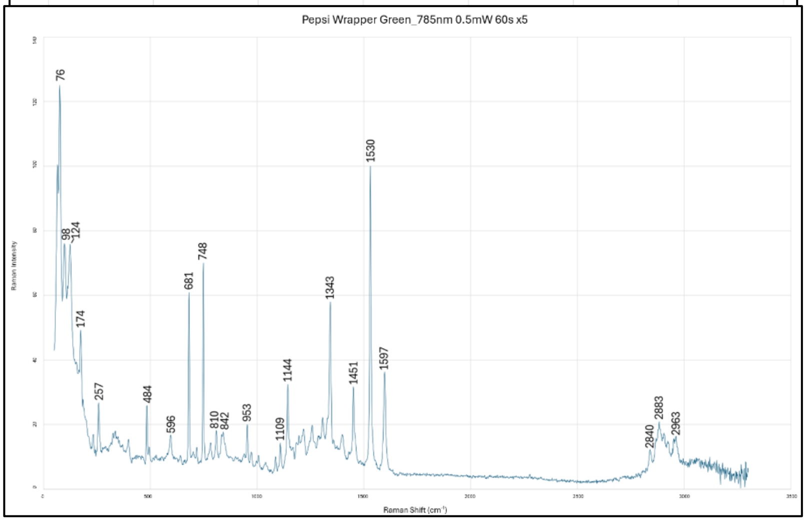

Marylands Wrapper Yellow_785nm 1mW 60s x3
Raman Intensity
Raman Shift (cm⁻¹)
106
172
398
453
531
616
809
841
900
939
973
998
1044
1151
1167
1219
1256
1287
1329
1359
1399
1436
1460
1523
1597
2816
2835
2885
2906
2960
3221

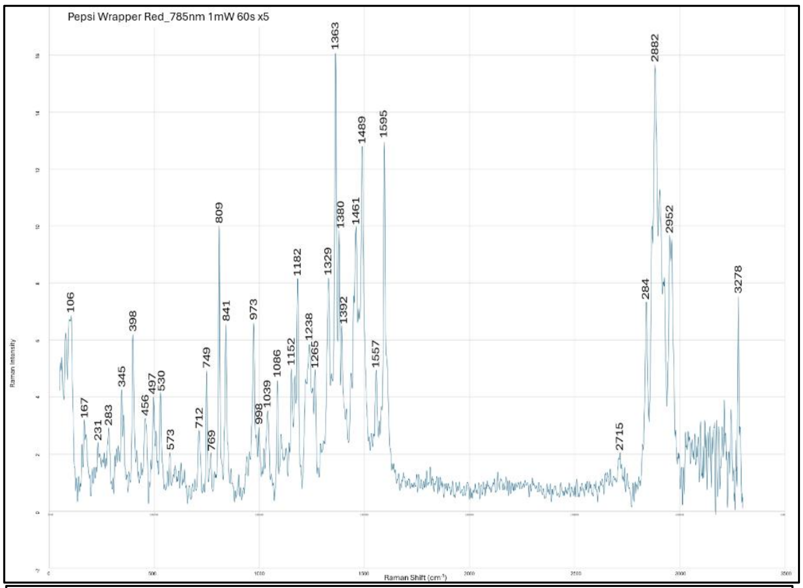

Pepsi Bottle_785nm 0.2mW 30s x3
Raman Intensity
Raman Shift (cm⁻¹)
631
70
859
1000
1096
1115
1175
1290
1417
1615
1727
296
308

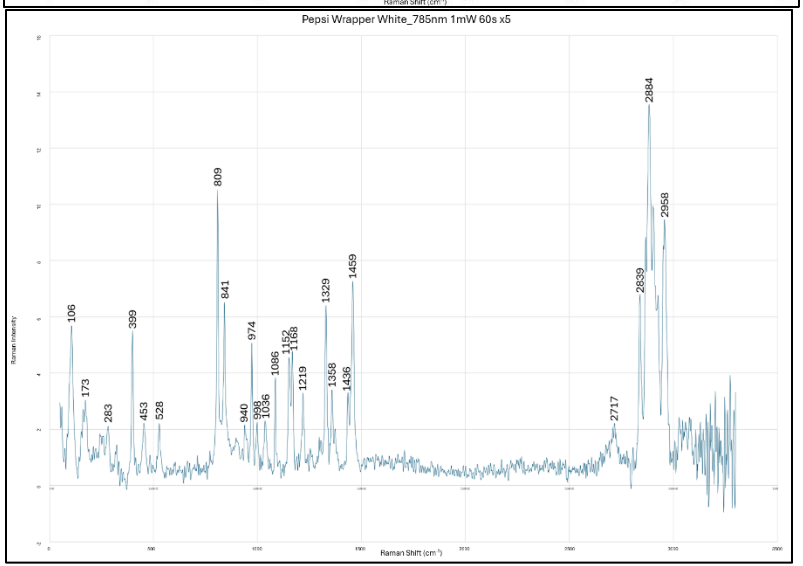

Pepsi Cap_785nm 0.5mW 45s x3
Raman Intensity
Raman Shift (cm⁻¹)
1062
1129
1169
1295
1416
1434
1461
2721
2848
2882

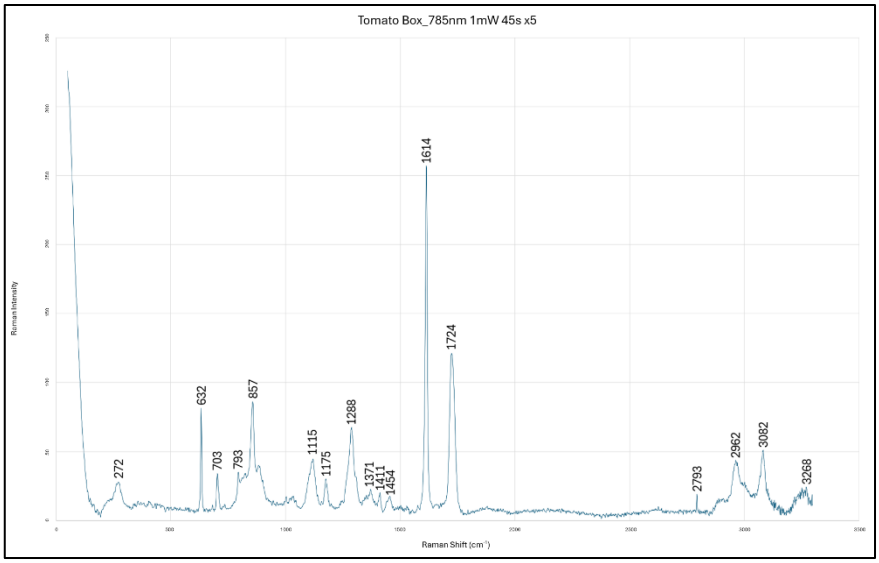

Pepsi Wrapper Black 2_785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
61
94
260
483
592
680
747
830
952
1109
1142
1217
1307
1339
1449
1525
1590
2358
2889
3073


Pepsi Wrapper Blue_785nm 0.5mW 60s x5
Raman Intensity
65
99
258
483
59
680
748
954
1008
1109
1144
1208
1256
1307
1342
1392
1431
1451
1529
2883
2963


Pepsi Wrapper Green_785nm 0.5mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
76
98
124
174
257
484
596
681
748
810
842
953
1109
1144
1343
1451
1530
1597
2840
2883
2963


Pepsi Wrapper Red_785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
106
167
231
283
345
398
456
497
530
573
712
749
769
809
841
973
998
1039
1086
1152
1182
1238
1265
1329
1363
1380
1392
1461
1489
1557
1595
2715
284
2882
2952
3278


Pepsi Wrapper White_785nm 1mW 60s x5
Raman Intensity
Raman Shift (cm⁻¹)
106
173
283
399
453
528
809
841
940
974
998
1036
1086
1152
1168
1219
1329
1358
1436
1459
2717
2839
2884
2958


Tomato Box_785nm 1mW 45s x5
Raman Intensity
Raman Shift (cm⁻¹)
272
632
703
793
857
1115
1175
1288
1371
1411
1454
1614
1724
2793
2962
3062
3268