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# WWU Using Raman Spectrometry to Identify Organic Contaminants Sorbed onto Plastics

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**Internship Title:** Using Raman Spectrometry to Identify Organic Contaminants Sorbed onto Plastics - Western Washington University

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**Internship Dates:** 1/4/2022 to 3/14/2022

**STUDENT SIGNATURE**

**DATE:** 3/14/2022

# Using Raman Spectrometry to Identify Organic Contaminants Sorbed onto Plastics

## Introduction

A spectrometer is used for the interactions between light and matter to create a spectrum detailing information such as chemical structure and concentration. Specifically, for the Raman Spectrometer used in this study, the Raman Shift ($cm^{-1}$), which is the energy difference between the incident light and the scattered light, is examined as a means to characterize chemical structure (Basics of Raman Spectroscopy, 2020). The goal of this internship was to determine if organic contaminants sorbed to plastics could be identified using the Raman spectrometer and if the spectrum would be able to indicate differences between the plastics and organic contaminants. This was done by soaking Nylon 6 polycaprolactam monofilament fishing line in a solution of water, methanol, and 4-tert-butylphenol at varying concentrations for several days before analyzing them under the Raman microscope.

## Methods

### *Fishing Line Experiment*

The 4-tert-butylphenol (TBP) solution was created by first adding 7.5mL of water and 7.5mL of Methanol into a 20mL capped vial. Each vial received roughly 100 mg of Nylon monofilament fishing line. The nylon fishing line used was Shur Strike monofilament with a 15lb test weight, it should be noted that this line was not sold for fishing but instead for the purpose of hanging decorations. A control vial was also created with no TBP present. Vials 2 through 4 had roughly 100, 200, and 500mg of 4-tert respectively (Table 1). These vials were then left to soak out of sunlight for 6 days before being analyzed under the Raman.

### *Raman Measurements*

Instrumental details of the Renishaw Confocal Raman microscope are as follows. For the laser source, a 532nm Nd:YAG laser was employed and calibrated following a standard operating procedure utilizing a polished metal slide.

All samples were measured using the 532nm laser with 1800 lines/mm refraction grating setting. The fishing line was taken out of the vials and cut to a workable size and placed on a glass slide, each end of the line was taped down to make sure no movement occurred while taking measurements. For the first set of spectral acquisitions the 50 X objective was used and the extended range was set from 100-3200 $cm^{-1}$ with a laser power of 5% for 10 seconds and 1 accumulation. This process was repeated for each vial as well as with the liquid from the 500mg vial. A second set of measurements were taken a month later as depth acquisitions, the same slide set up was followed as mentioned above. This time the 100x objective was used and extremely carefully as to not run the baseplate into the objective. Once the line was in focus it was then defocused slightly higher and an origin was set on the software. The depth series acquisition was selected in the measurement and 5 acquisitions were made with 10 µm spaced intervals. Laser power was set to 10% with 10 second exposure and the extended range was the same as previous 100-3200 $cm^{-1}$.

## Results and Discussion

Using the built-in library of plastics in the Wire 5.5 software the control line run was able to establish that the polymer being used was in fact Nylon 6, polycaprolactam (0.964 accuracy). The following two acquisitions originally appeared to be very similar to the control when looking at their spectrums on the Wire software with only minor differences and small changes to the quality that the program represented for matching to Nylon 6. All of the line acquisitions share similar peaks with the largest occurring just before 3000 cm$^{-1}$ and two of similar height at 1120 cm$^{-1}$ and 1441 cm$^{-1}$ (Figure 1-4). These are some of the key peaks which identify the material as Nylon 6. Figure 5 shows the liquid acquisition from the 500mg TBP vial and does not follow the trend of the previous figures since it does not have any nylon present, except possible trace amounts. Raman shifts likely belong to TBP were present in the acquisition. The most significant of these peaks are identified at 820 cm$^{-1}$, two at 1100 and 1112 cm$^{-1}$, 1600 cm$^{-1}$ as well as several around 3000 cm$^{-1}$ (Figure 5).

These initial results were discouraging since the Wire 5.5 Software did not include any organic contaminants in its library of spectrums. It was also difficult due to the overlap of peaks between the graphs of the line and the liquid which was used as the identifier of 4-tert. The more prominent peaks at 1100, 1112, 1600, and 3000 cm$^{-1}$, in figure 5 all corresponded with peaks on the line acquisitions and couldn't be used as identifiers. However, upon graphing the data in excel a small peak began to appear through greater concentrations at around 820 cm$^{-1}$ and was also present on the 4-tert identifier spectrum (Figure 5). This peak is also not present on the control spectrum meaning it can be ruled out as being caused by the methanol or water (Figure 1). The peak starts appearing noticeably on the 200mg spectrum and is drastically noticeable on the 500mg spectrum (Figures 3 and 4).

Upon discovering this peak another Raman measurement was taken, this time as a depth series acquisition, and intensity at the peak was graphed as well (Figure 6). This spectrum is different from the others as it comes directly from the Wire 5.5 software because it was not graphing correctly when done on excel. While there was only a 40 µm depth difference taken due to time limits it appears as though there could have been some uneven degradation of fishing line since the intensity changes drastically in only 15% of the full line's width. There could also be other errors associated with the intensity change since the depth function of the Raman has only recently been attempted here at Western Washington University.

**Table 1.** Amounts of fishing line, TBP, water, and methanol added to each vial.

| Vial # | Fishing line (mg) | 4-tert (mg) | Water (mL) | Methanol (mL) |
|---|---|---|---|---|
| 1 | 98.4 | 0 | 7.5 | 7.5 |
| 2 | 102.8 | 103.4 | 7.5 | 7.5 |
| 3 | 100.2 | 199.2 | 7.5 | 7.5 |
| 4 | 102.8 | 496.9 | 7.5 | 7.5 |

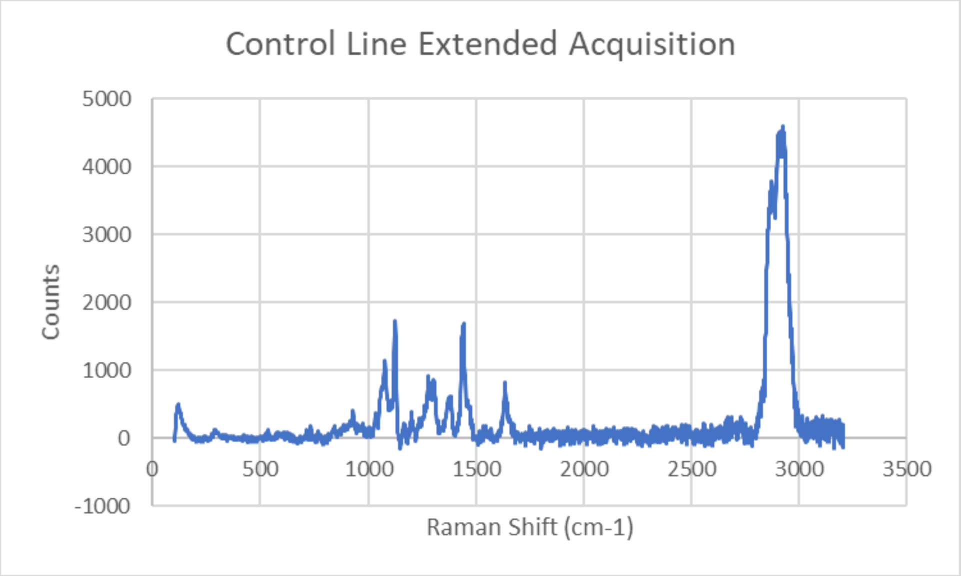

**Figure 1.** The extended range acquisition taken of the control vial fishing line. Showing as counts over Raman Shift (cm$^{-1}$) with subtracted baseline.

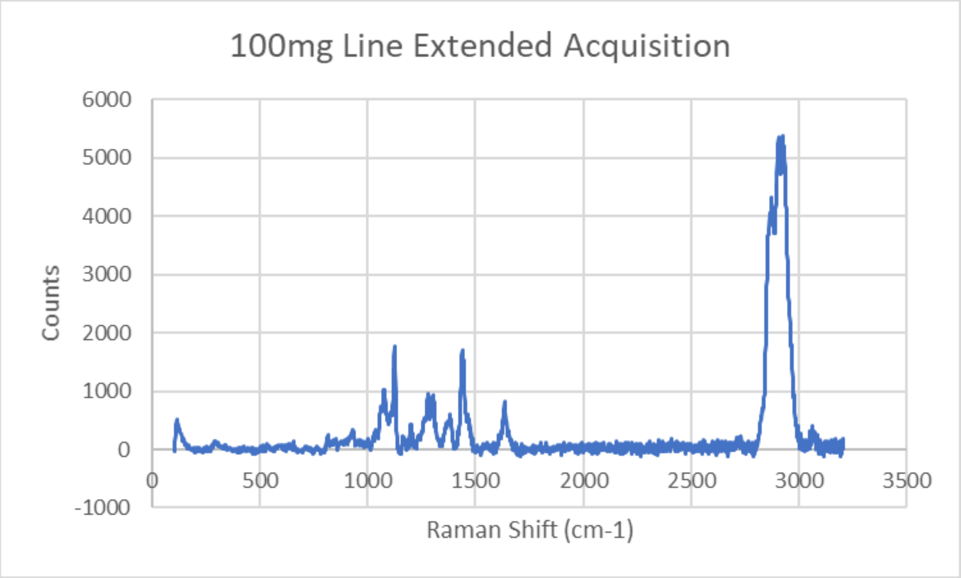

**Figure 2.** The extended range acquisition taken of the 100mg TBP vial fishing line. Showing as counts over Raman Shift (cm$^{-1}$) with subtracted baseline.

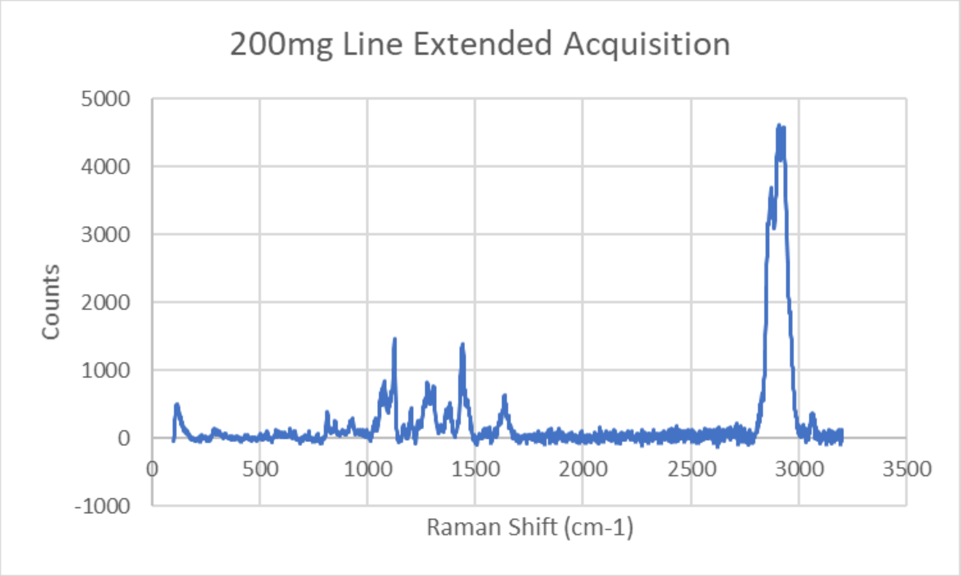

**Figure 3.** The extended range acquisition taken of the 200mg TBP vial fishing line. Showing as counts over Raman Shift (cm$^{-1}$) with subtracted baseline.

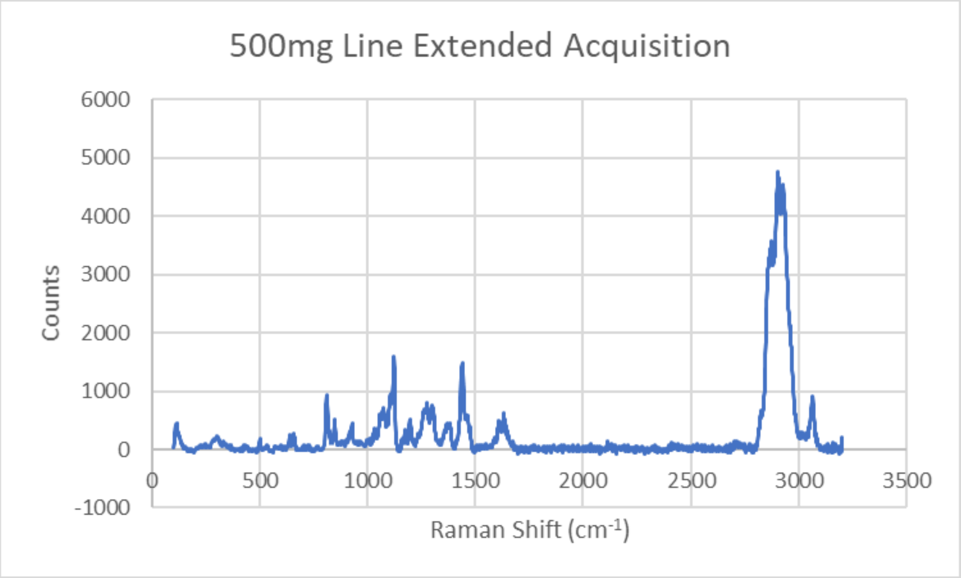

**Figure 4.** The extended range acquisition taken of the 500mg TBP vial fishing line. Showing as counts over Raman Shift (cm$^{-1}$) with subtracted baseline.

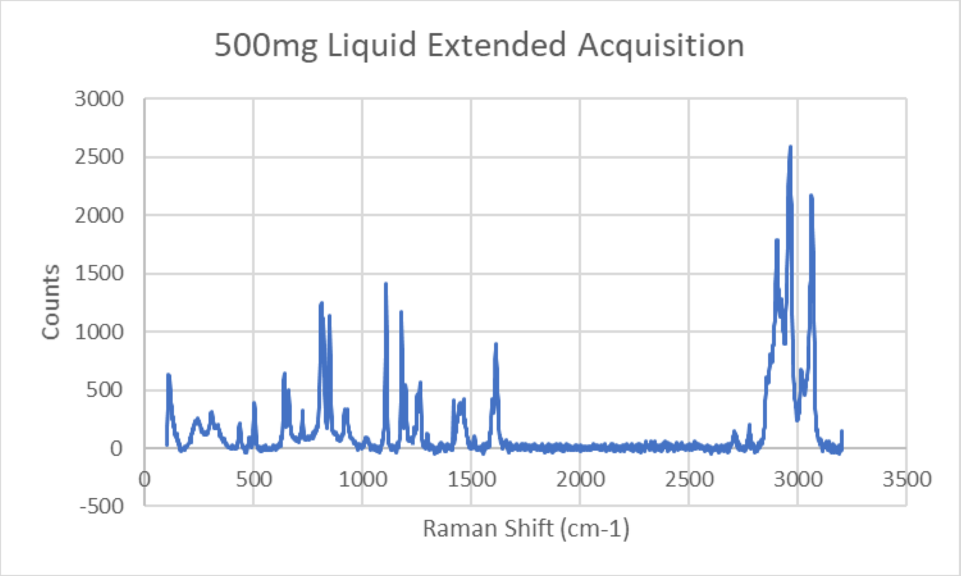

**Figure 5.** The extended range acquisition taken of the 500mg TBP vial liquid. Showing as counts over Raman Shift (cm$^{-1}$) with subtracted baseline.

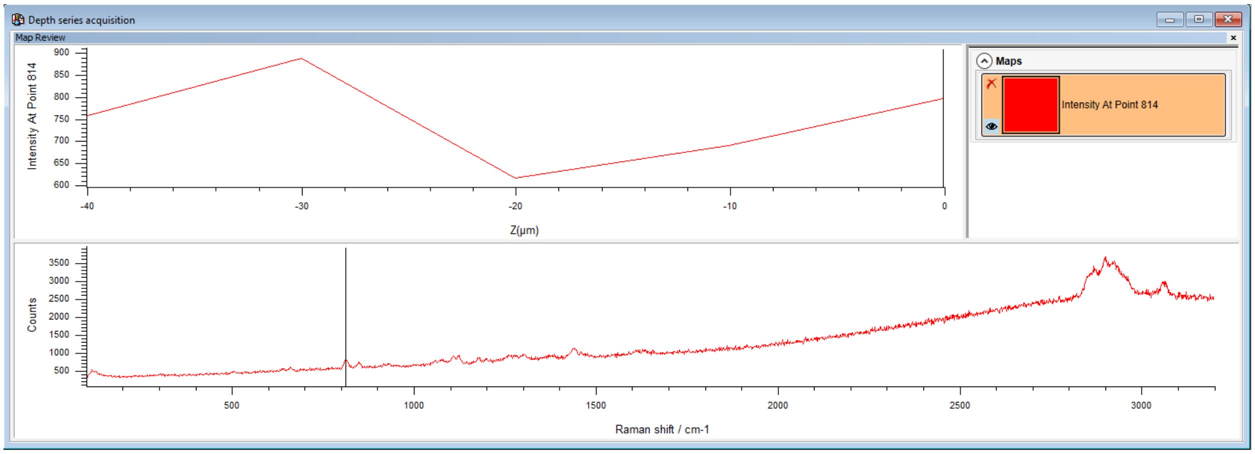

**Figure 6.** Lower is the extended range depth series acquisition taken of the 500mg TBP vial fishing line. Showing as counts over Raman Shift ($cm^{-1}$). Upper shows the intensity at the point $814cm^{-1}$ as it varies in depth Z (µm).

## Conclusion

The data collected from this study showed that it is possible to use Raman Spectrometry to identify organic contaminants sorbed on plastics. This is due to the peak at 800 $cm^{-1}$ appearing in the liquid spectrum and the line spectrums but not the control. While more tests should be run, especially with depth series acquisitions, this is a solid first step in showing that organic contaminants can be observed with the Raman and differentiated from the plastics they are sorbed to. In the future several samples of differing plastics and organic contaminants should be tested and should not be left soaking for as long in regards to the second measurement made after a month.

# References

*Basics of Raman Spectroscopy :: Anton Paar Wiki*. Anton Paar. (2020). Retrieved March 8, 2022, from https://wiki.anton-paar.com/us-en/basics-of-raman-spectroscopy/