Identification of Environmental Plastic Samples from a Caribbean Beach Survey by Near-Infrared Spectroscopy with the MicroNIR and Chemometric Analysis

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Abstract

MicroNIR is a portable near-infrared diffuse reflection spectroscope. Its suitability for identifying environmental plastic polymers was evaluated through a series of performance tests. The plastic samples were collected during a beach survey in the Caribbean. First a reference database was built by analysing a series of reference plastic polymers. Prediction models were constructed by using principal component analysis (PCA) and cluster analysis on 2D- and 3D-scatterplots. Measurements of samples with a surface area down to 1 mm² were successfully identified with the prediction models. Blend spectra were created by measuring two polymers simultaneously, from which each polymer NIR-fingerprint were able to be individually extracted from the blend spectra by subtracting the NIR-fingerprint of the opposite polymer. Prediction models were used to identify the samples in the tests with household plastics and the environmental plastic samples, collected in the Caribbean. Out of the forty-eight samples collected forty (83%) were identified. Twenty-seven were identified as polyethylene (56%), eleven as polypropylene (23%), one as polystyrene (2%), and one as polyamide (2%).

Key Terms: MicroNIR, Near-infrared spectroscopy, Chemometrics, Plastic polymer identification, Environmental plastic beach survey
Sammanfattning
MicroNIR är ett portabelt instrument som mäter nära infraröd reflektans. Instrumentets lämplighet för identifiering av plastprover insamlat från en strandundersökning i Karibien plastskräp, utvärderades via en serie av tester. Först konstruerades en databas genom analys av referensplast. Prediktionsmodeller skapades med principal komponent analys (PCA) och bearbetad data överfördes till en 2D- eller 3D scatterplot för visuell klusteranalys. Prediktionsmodellerna kunde med framgång identifiera mätningar tagna på prover med en yta av ner till 1 mm². Blandspektra skapades genom mätningar av två plasttyper simultant, vars enskilda NIR-fingeravtryck kunde extraheras via subtraktion av motstående polymerens NIR-fingeravtryck från blandspektrat. Prediktionsmodellerna användes för att identifiera prover i testerna med hushållsplaster och miljöplasterna från Karribien. Av de fyrtioåtta prover från Karribien, kunde fyrtio (83%) prov identifieras. Tjugosju identifierades som polyetylen (56%), elva som polypropylen (23%), en som polystyren (2%), och en som polyamid (2%).
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1. Introduction

1.1 Polymers

Since the early 1950s global production of plastics has increased rapidly from 1.7 to 299 million tons in 2013 (PlasticsEurope, 2015), consuming roughly 8% of the entire world’s oil production (Thompson et al., 2009). Since their introduction, plastics have become a fundamental part of modern society with many beneficial uses and can easily be manufactured at low cost to fit many different industrial and commercial needs.

The composition of plastics is usually that of an organic polymer containing carbon atoms with additional oxygen, sulphur, and/or nitrogen atoms depending on what type of plastic polymer it is (Figure 1). These form units that add up to make long chains. These chains make up the backbone of the polymer and from this chain additional molecular groups can be attached to customize the properties of the polymers. Some of the most common polymers are polyethylene and polypropylene, making up roughly 50% of all plastic products manufactured (Plastic-Europe, 2014/2015).

![Figure 1. Shows the molecular polymer structure of the three most common plastic polymers a) polyethylene b) polypropylene c) polystyrene](image)

Plastics have high durability, versatility, and longevity. With properties such as durability and longevity, plastics can pose an environmental problem if these products are not properly disposed of. Improper recycling, poor waste management, and sometimes deliberate littering have made plastics a large component of contaminating debris on land and in marine habitats, sometimes accounting for 40-80% of all debris contaminating some marine habitats (Derraik, 2002; Barnes, 2002). Plastic debris can enter marine environments through several different pathways. A few of which is migration from sources such as fly-tipping sites, sewage overflows, and from littering (Williams & Simmons, 1996; Sadri & Thompson, 2014). Plastic debris can be very long lasting with predictions of lasting up to thousands of years, and even longer in deep sea and polar environments (Barnes et al., 2009). Plastic debris degrade primarily through photo degradation, oxidation, and to lesser extent mechanical abrasion (Andrady, 2011). During their degradation the plastics become brittle and microcracks will form on the surface and small pieces will start to break off, yielding microplastic particles. These microparticles have chemical properties that lead them to accumulate toxic persistent organic pollutants (POPs). Further, these microparticles laced with POPs can be ingested by marine biota and negatively impact marine ecosystems on a global scale. Great efforts have been taken to reduce plastic waste contaminating the environment as more plastics is recycled and landfill tipping is getting more restricted in many nations (Plastic-Europe, 2014/2015). It is of significant value to monitor the movements of plastics debris in order to measure the efficiency of implemented political
actions made to reduce the abundance of plastic debris getting into various environments. As different polymers due to varying density, size, and other properties, will have different movement patterns in the environment, monitoring polymer identification would provide further insight in these movement patterns (Browne et al., 2010). Different polymers may have different hazardous effects on the environment (Lithner, 2011). Because of this, polymer identification may also be important from a risk assessment perspective. Surveying stranded plastic litter on beaches has been used as a method to monitor the abundance and movement of plastic debris in marine environments (Ryan et al., 2009). The exact movements of plastic debris is not fully understood as of to date. Analysis of plastic debris stranded on isolated beaches in Brazil, identifying plastic litter to be of urban origin, confirms the assumption that plastic debris can have far-reaching movement patterns in the environment (Araujo & Costa, 2007).

1.2 Analysis
There are a few different analytical techniques that can be used to identify plastic polymers. Different techniques are suitable depending on what is to be analysed. Some techniques can give data on specific additives such as gas chromatography (GC) for measuring plasticisers or inductive coupled plasma (ICP) for measuring metallic content in the plastic sample. Other techniques can be used to identify the polymer that the plastic material is made of. Transmittance Fourier transform infrared spectroscopy FTIR and Raman spectroscopy along with other infrared and near infrared spectroscopy can be used to identify different plastic polymers with good accuracy (Browne et al., 2010; Forrest, 2002). FTIR is a simple technique that can be used not only to find what polymer it is, but also if there is any contamination present in the plastic or if the plastic is a mix of several polymers.

1.3 Objectives
In this project a microNIR, a portable device that measure near infrared (NIR) absorbance, was evaluated for its applicability on samples from beach surveys to see if it could be used for polymer identification. NIR spectroscopy, through its relative simplicity, offers many advantages compared to other analytical techniques: it is non-destructive, fast, and inexpensive (Zhao & Chen, 2015).

- The objective of this study is to model and identify different standard reference plastic samples based on their NIR-spectra and to fit these materials on a PCA plot.
- Can samples of unknown plastic materials be identified based on their NIR-spectra using the generated chemometric prediction model created from the standard reference plastic?
- Is the MicroNIR a suitable instrument for identifying plastic polymers?
- Does the shape of the plastic sample effect the fingerprint of intensity of the signal? What is the size limit? How small can the measured sample be and still produce an NIR-spectra that can be identified with the prediction model.
- Do darker colours on samples affect its absorbance, ultimately affecting its NIR-spectra?
- Is it possible to measure two polymers simultaneously to create a blend spectra from which IR-fingerprints can be extracted and identified with the prediction model?
2. Theory

2.1 Quality control in plastic production
The value of a simple polymer analysis is evident in plastic production as a common problem is failed products. For different reasons either because of incorrect formulation or faulty mixing/processing, a plastic product may fail to meet its specifications. Polymer analysis is a valuable component within plastic production to detect product failure and to test the product quality. A large portion of failed products can be detected through a series of analytical tests, with IR and NIR spectroscopy being one of the easier methods to determine its polymer type. NIR is a simple analytical method used to see if the plastic product is faulty because of contamination. However, caution should be taken as the relative intensity of the absorbance at each wavelength can vary and shift compared to traditional transmission spectra such as FTIR (Forrest, 2002).

2.2 Infrared spectroscopy
Infrared IR-spectroscopy measures the absorbance at different wavelengths to find information of the molecular vibrations which in term can provide insights about the structure of the molecule. Light energy gets absorbed and cause stretching and bending of covalent bonds. The stretching vibration energy between two atoms will increase going from single up to triple bond (Langford, 2010). Furthermore, with increasing atom mass the stretching vibrational energy decreases. Since the absorbance varies specific to the atoms and the type of bond, functional groups can be identified. For instance, alcohols are going to have O-H stretching absorbance and carbonyl groups are going to have C=O stretching absorbance. In the end the NIR-spectra is going to generate bands that are specific to the structure of the molecule and its functional groups (Langford, 2010).

2.3 Data analysis
In order to identify an unknown sample a database of clean plastic standard samples of known polymer-structures must first be constructed based on their NIR-spectra (Forrest, 2002). NIR-spectra of unknown samples can then be identified by matching it with a reference in the database.

2.4 Environmental plastic litter
The amount of plastic polymers found as environmental waste is expected to be in proportion to how much of it is manufactured and discarded. Polymers such as polyethylene and polypropylene make up roughly half of the total amount of plastics produced annually (Plastic-Europe, 22/01/2015). Several plastic waste surveys confirm the relative abundances of several polymer to be in approximated proportion to what is manufactured, with about Polystyrene (25%) and polypropylene 20% (Gasperi et al., 2014; Sadri & Thompson, 2014). Polyethylene is an exception as it has been found to make up 40 % of plastic litter composition, which is 10 % higher than what is being manufactured (Plastic-Europe, 2014/15). An explanation to this could be that polyethylene, polypropylene, and polystyrene are all used for packaging to a large extent and that could be why they are so prevalent in the environment.
2.5 MicroNIR

The instrument used in this project is the MicroNIR 1700, which is a miniature NIR spectrometer manufactured by JDSU. It uses a linear variable filter (LVF) situated on top of a diode array detector that split incoming light into individual wavelengths (Figure 2). A diffuse reflection disk is used for the sample is placed on. The spectrometer integrates the light source from the diffuse reflection disk and gives an NIR-absorbance spectrum in the range between 950-1650 nm.

![Diagram of MicroNIR technology](image)

*Figure 2. Illustrates the principle of the LFV component on the MicroNIR. Figure adapted from JDSU product literature 2014.*

The MicroNIR is a portable tool that can analyse a wide range of different materials. It is a non-destructive technique meaning that it is possible to analyse the materials in their current state, with little to no sample preparation. Due to the portable nature of this device it is important to take into consideration primary factors such as measuring distance between the device and the sample, and placement of the sample under the spectrometer (JDSU, 2014).
3 Method

3.1 Sampling

Environmental plastic samples were collected from four different locations at Anguilla Sandy hill beach in March 2015 (Table 1; Figure 3). The samples were kept in four separate bags marked with their GPS and time of collection. Twelve samples from each of the four bags were selected for analysis. Samples were in different shapes; thread/rope, sheet, or lump/block shapes. For samples that were in block/lump or sheet form, samples with a side that had a surface area in the range of 225 mm$^2$ to 2mm$^2$ were selected for analysis. Samples that were larger than that were cut down to meet size specification, as they would otherwise not properly fit over the reflectance disc. Samples with a surface area smaller than 2mm$^2$ were not selected for analysis. Samples that were in thread, rope, or string form were balled up to an estimated size of 225mm$^3$ of a lose clew of threads placed on the reflectance disc. Samples were selected with no discrimination to colours; black coloured samples were included. All samples were photographed and labelled with site of collection (B1-B4) and the colour and shape of the sample.

Table 1. List of time and location of sample collection.

<table>
<thead>
<tr>
<th>Location</th>
<th>Label</th>
<th>Date of collection</th>
<th>GPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anguilla Sandy hill beach</td>
<td>B1</td>
<td>2015-03-08</td>
<td>18°13'24.7&quot;N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63°00'29.8&quot;W</td>
</tr>
<tr>
<td>Anguilla Sandy hill beach</td>
<td>B2</td>
<td>2015-03-08</td>
<td>18°13'17.4&quot;N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63°00'29.9&quot;W</td>
</tr>
<tr>
<td>Anguilla Sandy hill beach</td>
<td>B3</td>
<td>2015-03-09</td>
<td>18°13'17.4&quot;N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63°00'29.8&quot;W</td>
</tr>
<tr>
<td>Anguilla Sandy hill beach</td>
<td>B4</td>
<td>2015-03-09</td>
<td>18°13'24.7&quot;N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63°00'29.8&quot;W</td>
</tr>
</tbody>
</table>

Figure 3, Map showing the location of collected samples of plastic from Anguilla Sandy Hill Beach.
3.2 Instrument and IR-spectrum collection

The MicroNIR 1700 from JDSU were used in this project with a spectral range of 950-1650 nm. Measurements were taken over a 99% diffuse reflectance panel. Measurement and data collection were done through the MicroNIR spectrometer operating software from JDSU. Before measurements were taken, the instrument was allowed to warm up for 10 minutes. All measurements were done with an instrument temperature between 45-55°C. 100% background scan was done against the 99% diffuse reflectance standard followed with a zero dark scan with the instrument light turned off.

Twelve samples of the unknown environmental plastics samples were analysed from each of the four different sites. Each sample was analysed with a minimum of three times to account for the varying intensity of the bands.

3.3 MicroNIR settings and data calibration

Earlier studies have shown that diode array instrument can sometimes suffer signal noise at the beginning and end of the spectrum (De la Haba et al., 2014). For that reason wavelength ranges below 1100 nm and above 1560 nm were discarded in this project to eliminate signal noise.

Different settings of scanning interval and integration times were tested to find optimal settings, which were then to be used for all other analysis. An integration time of 12000 µs and 50 scans per second were found to be an appropriate setting. There is an intensity variance for the absorbance inherit in the analytical method (JDSU, 2014; Forrest, 2002). Because of this, the data from each spectrum was normalized in relation to its own intensity by dividing the absorbance at each wavelength with the total absorbance at all wavelengths (Equation 1 & 2). This allows a NIR-band fingerprint to be obtained in spite of the varying intensity, since it is only the relation between each wavelength that is of interest for an NIR-fingerprint, not the specific intensity itself.

Equation 1

\[
\sum_{\lambda=1100}^{1560} \frac{Absorbance_{\lambda}}{Absorbance_{\lambda=1100}} = Absorbance_{\lambda=total}
\]

The total absorbance is obtained by adding the absorbance for all measured wavelengths (\(\lambda\)).

Equation 2

\[
\frac{Absorbance_{\lambda}}{Absorbance_{\lambda=total}} = Absorbance_{\lambda=relative}
\]

By dividing the absorbance at each wavelength (\(\lambda\)) with the total absorbance of all wavelengths, the relative absorbance for each \(\lambda\) is obtained.
3.4 **Chemometric data-treatment**

The data was pre-treated with standard normal variate (SNV) transformation, and then analysed with multivariate statistical software SIMCA from Umetrics. A principal component analysis (PCA) were done for all samples and checked in a 2D-scatter plot. In some cases a 3D-scatter plot was used as this will often give to understandable models compared to two-way methods that have a tendency to mix variables and give models that are harder to interpret (Lillhonga & Geladi, 2011).

3.5 **Model development, testing and sample analysis**

A number of clean standard plastics from Goodfellow Cambridge Limited in Huntingdon PE29 6WR England (Table 2) were used to create a database. Ten measurements of each standard reference plastic in granule form and three measurements of each in powder form were analysed and designated as calibration set samples for model development. For model verification a number of household plastics marked with plastic resin identification codes for polystyrene (6) and polypropylene (5). The household plastics were measured three times and put through the same mathematical pre-treatment as all other samples and then put in the chemometric prediction model.

Three prediction models were constructed in SIMCA by doing a 2D- and a 3D-scatterplot. The first prediction model excluded data from the PHB, PET, and the powder samples of PS, PA, and UPVC (Figure 4 a). The second model excluded PP, PE, and the powder samples of PA, PS, and UPVC (Figure 4 b). The third model included the powders but excluded all reference plastic samples in granule shape (Figure 4 c). The models were implemented as such that the unknown sample would be matched with the first model. If the unknown sample was successfully matched with one of the unique polymers such as PP, PE, and PS, then no further analysis was necessary. If however the unknown sample was matched with a biopolymer or one of the similar polymers, then the unknown sample was put into the second model to find which specific polymer matched best with the sample. If still no match was successful, then the unknown sample would be put in the third model. If still no match could be made, then the sample was marked as unidentified. This was done for all forty-eight unknown samples and the three household samples used for model verification.

*Table 2. List of clean plastic polymer reference materials.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Shape</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>PE</td>
<td>Granule</td>
<td>3mm</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>Granule</td>
<td>3mm</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>Granule</td>
<td>NAN</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>Powder</td>
<td>950 micron</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>Powder</td>
<td>250 micron</td>
</tr>
<tr>
<td>Polyhydroxyalkaonate - Biopolymer</td>
<td>PHA</td>
<td>Granule</td>
<td>3mm</td>
</tr>
<tr>
<td>Polyhydroxybutyrate - Biopolymer</td>
<td>PHB</td>
<td>Granule</td>
<td>5mm</td>
</tr>
<tr>
<td>Polylactic acid - Biopolymer</td>
<td>PLLA</td>
<td>Granule</td>
<td>5mm</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>Granule</td>
<td>3mm</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>PET</td>
<td>Granule</td>
<td>3mm</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>PA6</td>
<td>Powder</td>
<td>350 µm</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>PA6</td>
<td>Powder</td>
<td>15-20 µm</td>
</tr>
<tr>
<td>Polyvinylchloride unplasticised</td>
<td>UPVC</td>
<td>Powder</td>
<td>250 µm</td>
</tr>
</tbody>
</table>
Figure 4 (a). This is a 2D-scatterplot of the first prediction model used to match PA, PC, PE, PP, PHA, and PS.

Figure 4 (b). This is a 2D-scatterplot of the second prediction model used to match PC, PET, PHA, PHB, PLLA, and PS, in those cases the first prediction model failed to make a match.

Figure 4 (c). This is a 2D-scatterplot of the third prediction model used to match PA, PS and PVC in those cases the first and second prediction model failed to make a match.
3.6 Sample size limit test

Sample size limitation of the MicroNIR 1700 was tested by measuring ten samples of PP that were cut to ten different sizes of decreasing surface area. Size was measured judged by measuring the surface area of the face turned to the MicroNIR during analysis. The thickness of the sample were not carefully considered, but were roughly around 1 mm. Surface area ranged from 100mm$^2$ down to 0.36mm$^2$. A complete list of the different sizes can be found in Appendix 3. The data was then analysed to see if the model could still recognize the NIR-spectra.
4 Results

4.1 Data normalization

As have been mentioned in other studies and in literature, the intensity of the NIR-band can vary (JDSU 2014; Forrest, 2002). Although the NIR-fingerprint for each of the different plastic polymer was nearly identical, the intensity of each NIR-fingerprint would differ. When overlapping the spectra from different samples of the same clean standard polymer, it became evident that the intensity of the different samples would vary, up to several hundred percent in worst cases (Figure 5).

Figure 5. a) Shows the NIR-spectra of a number of samples (polyethylene) with the absorbance on the y-axis and wavelength on the x-axis. Each NIR-band represents a different sample showing the absorbance at each wavelength from 900 nm to 1670 nm for each sample. The different pellets from the same batch of reference plastic share similar spectra the intensity however is shown to vary. B) Shows the NIR-spectra of a number of samples of polypropylene. Polypropylene has a distinct spectra and similar to polyethylene it varies in absorbance intensity, but to a lesser extent.

The relative proportions between the absorbance at different wavelengths still remain roughly the same regardless of the intensity. So by applying equation 1 & 2, which gives the relative absorbance at each wavelength, the NIR-fingerprint moved closer to each other (Figure 6).

Figure 6. These two spectra (polyethylene & polypropylene) are constructed from the same measurements as in figure 5. However, in these IR-spectra equation 1 & 2 have been used to reduce the impact of the varied intensity between samples. The spectra show the relative absorbance for each sample, resulting in a cleaner overlap of the different fingerprints.
4.2 **MicroNIR settings**

Different settings were tested in order to find optimized settings for the analysis of polymer IR-fingerprints (Figure 7). The figure showcase the results after analysing the same plastic pellets of polypropylene with four different settings of integration time (IT) and the number of scans per second (s). At lower integration times around 10000 µs, disturbances at wavelengths <1150 nm were more common as can be seen in figure 3 (a). Another phenomenon was observed with progressively higher IT where the absorbances at higher wavelengths would get more saturated. The effect of this would cause the line representing absorbance at higher wavelengths to get dragged down closer toward the x-axis. This is illustrated in figure 3 (b) to (d) where wavelengths over 1500 nm were getting saturated and therefore dragged down toward x-axis. At IT higher than 20000 µs the line at higher wavelengths would lay completely flat against the x-axis. The higher and lower IT also seem to induce more variance of the intensity of the absorbance at all wavelengths compared to IT between 10000-12000 µs illustrated by figure 3 (b) and (c). Based on these findings a decision was made to run the samples at a setting of 12000 µs IT and 50 scans per second.

![Figure 7](image)

*Figure 7. Different settings were tested to find suitable integration time measured in µs and number of scans per second. (a) Illustrates that with shorter IT there might be risk of disturbances at wavelengths <1150 nm. (b) and (c) show less disturbances but (c) show that with longer IT wavelengths >1500 nm are getting saturated and thus dragged toward the x-axis. (d) shows that this phenomenon increases at longer IT.*
4.3 Determining wavelength ranges

Earlier studies have shown that diode array instrument such as the MicroNIR 1700 can suffer signal-noise at the beginning and end of the spectrum (Haba et al., 2014). This was seen in the previous figure (Figure 7) where in spite of what setting some polymer NIR-fingerprints still retained a lot of disturbances at wavelengths below 1100 nm and above 1500 nm. Additional small peaks would appear, seemingly randomized at these high and low wavelengths. Though some peaks would be shared between the samples, many of them would not. Indicating that these peaks were not part of the polymers characteristic fingerprint. Not all polymers suffered from this problem. While some polymers were found to have relatively clean fingerprints, others suffered disturbances at the beginning and end of the wavelength-range of the NIR-spectra. Polymers such as polystyrene, polyethylene, PET, PHA, and PHB in particular were often found to have a lot of randomized peaks at wavelengths <1150 nm which can be seen in the left NIR spectra in (Figure 8 a & b). New spectra were constructed excluding the areas with high disturbances and can be seen in the right NIR-spectra in (Figure 8 a & b). These NIR-spectra show two polymer NIR-fingerprints that were found to have a lot of disturbances at shorter wavelength. By excluding the regions with the most background-noise, the fingerprints from the different samples of the same plastics became more even, closer together, and did not differ from each other to any large extent.

![Graphs showing NIR-spectra of polystyrene and PHB granule](image)

Figure 8. (a) Shows the NIR-fingerprints of polystyrene before (left) and after (right) the exclusion of the wavelengths <1100 nm and >1560 nm. It illustrates the problem of unexplained and randomized peaks at the lower end of the spectra <1150 nm. The NIR-spectra without these regions show much clearer fingerprints. (b) Shows the NIR-spectra of the plastic that had the most variation and disturbances in this study, PHB. After the exclusion of the regions <1100 nm and >1560 nm the fingerprints are now more clear and they resemble each other more.
4.4 Multivariate statistical analysis

Most of the plastic fingerprints were able to be separated with the use of multivariate statistical program SIMCA. A 2D-scatterplot was sufficient to separate most of the plastics (Figure 10). But for similar plastics that unfortunately also have a lot for variation in the absorbance intensity, such as the biopolymers PHA, PHB, PLLA, were difficult to separate. PET was difficult to separate from PS and PC. Better separation was achieved in a 3D-scatterplot where all plastics could be separated (Figure 11).

![Figure 10](image1.png)

**Figure 10.** This is a 2D-scatterplot contain all reference plastic samples where different plastics have been separated and grouped by their characteristic NIR-spectra. Data was pre-treated with standard normal variate (SNV). Each colour and shape combination represents different reference plastics. The closer the value in the scatterplot, the closer their NIR-spectra resembles each other. Clusters are formed as similar NIR-spectra are grouped together. The trend seems to be that similar plastic polymer cluster closely together. The polyamide (PA) samples represented by the red squares, blue and green circles cluster closely together in the upper right corner of the 2D-scatterplot. Similar phenomenon can be observed for the bio-polymers.
Figure 11. This is a 3D-scatterplot made from the same data as the 2D-scatterplot in figure 10. Data was pre-treated with standard normal variate (SNV) transformation. In this 3D-scatterplot better separation can be achieved because three components are included in the calculations.

However, there was still a lot of variation making conclusive identification of plastics difficult with this model. As explained earlier in the method section 3.5 (Figure 4 a-c) the standard NIR-spectra were divided into three models used to identify the unknown samples. The first model excluded all polymer standard powders and only included one of the bio-polymers. The second model included all biopolymers and PET but excluded polymers PP and PE. The third model only included the polymer standard powders. The unknown sample was first put in the first model to see if it would cluster with any of the reference plastics in the model. If a match was made with the biopolymer, then the unknown sample would be put in the second model to identify which of the biopolymers matched best. If still no match were successful in the second model, it would be put in the third model, and if no match was met, the sample was considered unidentified.

The accuracy of the match was confirmed with a visual comparison of the spectra.
4.5 Model testing

Two different household plastics of known polymer composition were analysed and correctly matched in the model (Figure 12 & 13).

**Figure 12.** One plastic food container of Polystyrene (PS) was correctly matched as PS in the first model constructed for this project. The plastic food container is represented by the black triangle and it matches with the light blue cluster of polystyrene reference sample.

**Figure 13.** One plastic container of polypropylene (PP) was correctly matched as PP in the first model constructed for this project. The plastic container is represented by the black triangle and it matches with the dark green cluster of polypropylene reference plastic.
4.6 Environmental plastic composition

Most of the environmental samples from the beach survey could be identified (Table 3). Of the forty-four unknown samples 17% remained unidentified. Twenty-five of the samples were identified as polyethylene (56%) and eleven of them polypropylene (23%). Less common polymers were polystyrene (2%) and polyamide (2%), one of each was found. The matching in the first and second model was good in a majority of the samples (Appendix 2). Regarding the unidentified samples, there was some indication that a few of them might have been polystyrene, as they had similar NIR-fingerprints. However, the matchup where not strong enough with any of the models constructed in this project to make that claim so they remained labelled as unidentified.

Table 3. Lists the unknown samples with their place of collection and identification-tag to the left. Their respective polymer match according to model 1 & 2, and colour. Sample matching with PCA-models and images can be found in (Appendix 2).

<table>
<thead>
<tr>
<th>Location, sample</th>
<th>Matched polymer</th>
<th>Colour of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1, sample 1</td>
<td>PE</td>
<td>Blue</td>
</tr>
<tr>
<td>B1, sample 2</td>
<td>PE</td>
<td>Light blue</td>
</tr>
<tr>
<td>B1, sample 3</td>
<td>PE</td>
<td>Light yellow</td>
</tr>
<tr>
<td>B1, sample 4</td>
<td>PE</td>
<td>Yellow</td>
</tr>
<tr>
<td>B1, sample 5</td>
<td>PE</td>
<td>Light blue</td>
</tr>
<tr>
<td>B1, sample 6</td>
<td>PP</td>
<td>Pink</td>
</tr>
<tr>
<td>B1, sample 7</td>
<td>Unidentified</td>
<td>Black</td>
</tr>
<tr>
<td>B1, sample 8</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B1, sample 9</td>
<td>Unidentified</td>
<td>Blue</td>
</tr>
<tr>
<td>B1, sample 10</td>
<td>PP</td>
<td>Green</td>
</tr>
<tr>
<td>B1, sample 11</td>
<td>PE</td>
<td>Red</td>
</tr>
<tr>
<td>B1, sample 12</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B2, sample 1</td>
<td>PE</td>
<td>Blue</td>
</tr>
<tr>
<td>B2, sample 2</td>
<td>PP</td>
<td>Blue</td>
</tr>
<tr>
<td>B2, sample 3</td>
<td>PE</td>
<td>Blue</td>
</tr>
<tr>
<td>B2, sample 4</td>
<td>PP</td>
<td>Blue</td>
</tr>
<tr>
<td>B2, sample 5</td>
<td>PE</td>
<td>Blue</td>
</tr>
<tr>
<td>B2, sample 6</td>
<td>Unidentified</td>
<td>Green</td>
</tr>
<tr>
<td>B2, sample 7</td>
<td>PE</td>
<td>Yellow</td>
</tr>
<tr>
<td>B2, sample 8</td>
<td>PE</td>
<td>Dark blue</td>
</tr>
<tr>
<td>B2, sample 9</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B2, sample 10</td>
<td>PP</td>
<td>White</td>
</tr>
<tr>
<td>B2, sample 11</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B2, sample 12</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B3, sample 1</td>
<td>PE</td>
<td>Blue</td>
</tr>
<tr>
<td>B3, sample 2</td>
<td>PE</td>
<td>Light green</td>
</tr>
<tr>
<td>B3, sample 3</td>
<td>Unidentified</td>
<td>Green</td>
</tr>
<tr>
<td>B3, sample 4</td>
<td>PE</td>
<td>Green</td>
</tr>
<tr>
<td>B3, sample 5</td>
<td>PP</td>
<td>Yellow</td>
</tr>
<tr>
<td>B3, sample 6</td>
<td>PE</td>
<td>Yellow</td>
</tr>
<tr>
<td>B3, sample 7</td>
<td>PS</td>
<td>Orange</td>
</tr>
<tr>
<td>B3, sample 8</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B3, sample 9</td>
<td>Unidentified</td>
<td>White</td>
</tr>
<tr>
<td>B3, sample 10</td>
<td>PP</td>
<td>Dark blue</td>
</tr>
<tr>
<td>B3, sample 11</td>
<td>PP</td>
<td>Red</td>
</tr>
<tr>
<td>B3, sample 12</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B4, sample 1</td>
<td>Unidentified</td>
<td>Blue</td>
</tr>
<tr>
<td>B4, sample 2</td>
<td>PA</td>
<td>Brown</td>
</tr>
<tr>
<td>B4, sample 3</td>
<td>PP</td>
<td>Yellow</td>
</tr>
<tr>
<td>B4, sample 4</td>
<td>PE</td>
<td>Light blue</td>
</tr>
<tr>
<td>B4, sample 5</td>
<td>Unidentified</td>
<td>Black</td>
</tr>
<tr>
<td>B4, sample 6</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B4, sample 7</td>
<td>PP</td>
<td>White</td>
</tr>
<tr>
<td>B4, sample 8</td>
<td>PE</td>
<td>White</td>
</tr>
<tr>
<td>B4, sample 9</td>
<td>Unidentified</td>
<td>Brown</td>
</tr>
</tbody>
</table>
4.7 Collecting spectra from a mixture of plastic polymers

When measured separately, PP and PS have their own distinct NIR-spectra (Figure 14).

![Figure 14: NIR-spectra of PP and PS](image)

But when measured together with 50-50 % proportions by measuring one 8x9mm sample of PP alongside one 8x9 mm sample of PS, a blend NIR-spectra is achieved (Figure 15).

![Figure 15: NIR-spectra of PP and PS 50-50%](image)

A series of measurements were done where the proportions between PP and PS were incrementally shifted from 100% PS to 100% PP (Figure 16). The results shows that by gradually decreasing the amount of PS in the sample, while increasing the amount of PP, the mixed NIR-fingerprint will gradually shift from a typical PS NIR-fingerprint to a typical PP NIR-fingerprint. The NIR-spectra...
seemed to reflect the relative proportions of each polymer, meaning that when there is a high proportion of PS, the PS NIR-fingerprint get stronger and vice versa for PP.

Figure 16. The proportions of Polystyrene (PS) and polypropylene (PP) were incrementally shifted from 100% PS and 0% PP at the top of the NIR-spectra, down to 0% PS and 100% PP at the bottom of the NIR-spectra. The NIR-spectra have been superimposed onto the same NIR-spectra, with the NIR-fingerprints spatially separated in the NIR-spectra to illustrate the gradual change from a PS IR-fingerprint to a PP NIR-fingerprint.
4.7.1 Extracting from blend IR-spectra

When having a NIR-spectra with an NIR-fingerprint composing of a mix of polypropylene (PP) and polystyrene (PS) as shown in the previous figure (Figure 15). It was found to be possible to extract each individual polymer NIR-fingerprint from the blend spectra by subtracting the other NIR-fingerprint (Figure 17 & 18). A polystyrene NIR-fingerprint was obtained by subtracting a polypropylene fingerprint from the blend spectra. However, it was found that often one cannot simply subtract any simple NIR-fingerprint from the bland spectra in question and expect the NIR-fingerprint from the other polymer to emerge. Since the intensity and also the relative intensity of the absorbance at each wavelength will often vary between measurements, it was found that it is often required to subtract or peel of a proportionally sized fingerprint in relation to the intensity of the particular multispectral in question for the other NIR-fingerprint to emerge.

![PPPS A - PS A](image1)

*Figure 17. By taking the blend spectra from figure 11 and subtracting the IR-fingerprint of PS, the other NIR-fingerprint of PP emerged.*

![PPPS - PP*3](image2)

*Figure 18. By taking the blend spectra from figure 13 and subtracting the IR-fingerprint of PP, the other NIR-fingerprint of PS emerged. However, in this case the absorbance intensity of PS was stronger than that of PP. The NIR-fingerprint of PP had to be multiplied by a factor of three before the subtraction was strong enough to produce a relatively clean PS NIR-fingerprint.*
The NIR-fingerprint of PS and PP extracted from the blend spectra was then put into the model and was correctly matched and identified as PS and PP with the use of the first model (Figure 19 & 20).

**Figure 19.** The extracted PP NIR-fingerprint from the multispectral was successfully identified as PP with the use of the first model.

**Figure 20.** The extracted PS NIR-fingerprint from the multispectral was identified as PS with the use of the first model.
4.8 Sample size limit test

The model was successful at identifying polypropylene samples down to a surface area size of 1mm² (Figure 21 & 22). A complete list of NIR-spectra from samples with a surface area ranging from 100mm² down to 0.36mm² can be found in (Appendix 3).

![Sample surface area 1x1mm](image)

*Figure 21. This is the NIR-spectra of PP cut down to a surface area of 1x1 mm. This was the smallest sample size that could be successfully measured and matched with the model in SIMCA.*

![Diagram](image)

*Figure 22. The NIR-spectra of the sample with 1 mm² surface area was successfully identified as PP with the model in SIMCA. Samples with smaller surface area were not successfully identified.*
5 Conclusions & Discussion

Better results were obtained through mathematically pre-treating the data by using the relative absorbance at each wavelength in relation to the total absorbance. This reduced the problem of varying absorbance intensity as was demonstrated in (Figure 5 & 6). Settings should be optimized to reduce background noise while not saturating the instrument. Integration time and numbers of scans per seconds can be altered to find a method that works well for the specific analysis.

A problem encountered during this project was background noise at the beginning and end of the NIR-spectra. This has been observed during previous studies with diode array instruments such as the MicroNIR. It might be a good approach to exclude the data near the beginning and end of the spectrum unless specific characteristic IR-fingerprint peaks are located at the edges of the NIR-spectra. This approach was tested with good success in this project as better IR-fingerprint was achieved this way.

It was found that a good method for identifying polymers is to construct prediction models with the use of multivariate statistical software. In this project multivariate statistical software was used to treat the data and construct prediction models. This was done by creating a database of known polymers which could then be used to match NIR-fingerprints from unknown samples with NIR-fingerprints from standard sample polymers. This proved to be a reliable method for identifying the polymer of most unknown plastic samples. The results by analysing the unknown plastic debris from the Caribbean beaches are presented in (Table 3). The composition of the forty-eight samples of plastic debris found reflects the finding from previous surveys. Polyethylene was the most common polymer found composing 56% of the analysed particles followed by polypropylene at 23%. Polystyrene was only found at 2% which is relatively low compared to other surveys where polystyrene is usually found at 10-20 %. A possible explanation for the lower occurrence of polystyrene might be explained by the unidentified samples. Some of the unidentified samples had NIR-fingerprints similar to polystyrene but the matching was not strong enough to separate the NIR-fingerprint from the bio-polymers with resembling NIR-fingerprints. It is possible that the actual occurrence of polystyrene was higher than the 2% that was identified in this project. Polyamide was found at 2%. A total 17% of the samples were not able to be identified.

There was indication that dark colour of the sample had an adverse effect on measuring. In particular, black samples were very much affected, giving very high absorbance at all wavelengths within the NIR-range and would drown out most of the NIR-fingerprint. The results from the black samples were not good enough to make a conclusive identification. However, while no match could be made in SIMCA with the black samples it was still possible to get a rough estimate of what polymer it could be. It is possible that the technique can be used to rule out certain polymers with drastically different NIR-fingerprints, but not confirm any particular polymer.

The MicroNIR was found to be able to successfully measure samples of polystyrene with a surface area down to 1mm² and still produce sufficient data to correctly identify samples of this size. The MicroNIRs performance to measure other small sample of polymers was not explored during this project. Future studies should focus on examining the limit for each polymer more closely since it’s very important to know the limits of the measuring instruments used for these types of environmental surveys. The MicroNIR shows good potential for use in environmental plastic surveys.
An interesting finding during this project was the extraction of single polymer NIR-fingerprint from a blend spectra with data collected by measuring two polymers at the same time. PP and PS was first measured separately to obtain their respective NIR-fingerprint. Then a measurement was done with both of the polymers together with a 50-50 ratio. A blend NIR-fingerprint was obtained. And from that, each of the respective NIR-fingerprint was successfully extracted from the blend NIR-spectra by subtracting one or the other. Here is a simplified mathematical illustration of this:

\[
PP + PS = PPPS \\
PPPS - PS = PP \\
PPPS - PP = PS
\]

PP is measured together with PS, giving a PPPS IR-spectra. By taking PP NIR-spectra from a database and subtracting it from PPPS, the PS NIR-fingerprint emerges, and vice versa. Each of the extracted NIR-fingerprint was then successfully matched and identified as PP and PS with the prediction model constructed during this project. However, one should expect that the relative intensity of the absorbance might differ between the measurement of the blend NIR-spectra and the NIR-spectra from the standard samples. Because of this, it might be necessary to amplify or decrease the NIR-fingerprint that is to be subtracted before a clean NIR-fingerprint from the other polymer will emerge. Also, because of the varying intensity of the absorbance, it might be necessary to calculate the relative absorbances at each wave length relative from the total absorbance from both the blend spectra and the standard NIR-spectra together. Doing this will normalize the data and will improve matchup in the polymer identification model. One negative aspect of doing this is that it is very time consuming. But with proper programming software it might be able to be automated and therefore be less time consuming. This has potential to be used in both environmental surveys and quality analysis during plastic manufacturing as one common problem is that some plastics can be made from a mix of polymers. The potential of analysing blends of polymers with such a simple measuring device could be very useful.

Polypropylene and polystyrene was measured together with different blends of varying concentrations of both polymers (Figure 16). It was shown that the relative contribution of each IR-fingerprint to the blend NIR-spectra was in proportion to the amount of each polymer in the sample i.e. if there was more PP than PS in the sample, the PP NIR-fingerprint would tend to be stronger in relation to the PS NIR-fingerprint. This could be an indication that the absorbance-signal from either polymer is additive. Which the author of this report would claim is an additional optimistic indication that mixes of polymers could be analysed and have each polymer successfully identified.

There is room for improvements. Other mathematical pre-treatments could have been used. As mentioned, parts of the beginning and the end of the NIR-spectra were excluded due to signal-noise. There are however methods such as the Savitzky Golay smoothing filter that might have been able to reduce a lot of the signal-noise at these ranges. These ranges could possibly have been included and added to the NIR-fingerprint and give a better separation between some of the polymers.

Cross-validation error was not calculated for any of the NIR-fingerprints. This could have been used to spot and exclude outliers. In this project, every measurement was included and as such, outliers might have negatively affected the results.
6 Acknowledgements

I express sincere thanks to my supervisor Therese Carlsson for the expertise and guidance through this project.

I thank Malin Karlsson, Elisabeth Ängmyren, Cecilia Hagberg, Sofie Björklund, Carl Remmer, Theolinda Hanell, Bella Berg, and the rest of the MTM-family for being company over the many late hours spent at the University working with our own respective projects.

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7 References


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8. Appendix

8.1 Reference plastic NIR-spectra

NIR-spectra of reference plastic polymer used in the database for this project.

NIR-spectra of Polystyrene (PS)

NIR-spectra of low density polyethylene (LDPE).
NIR-spectra of polycarbonate (PC).

NIR-spectra of polyethylene (PE).

NIR-spectra of polypropylene (PP).
NIR-spectra of a SIMCA reference polypropylene (PP).

NIR-spectra of Polylactic acid (PLLA).

NIR-spectra of PET, PEPT
NIR-spectra of Polyethylene terephthalate (PET)

NIR-spectra of Polyhydroxyalkaonate (PHA).

NIR-spectra of Polyhydroxybutyrate (PHB).

NIR-spectra of Polyhydroxybutyrate (PHB).
NIR-spectra of Polyvinylchloride unplasticised (UPVC).

NIR-spectra of polystyrene (PS) in powder form.

NIR-spectra of polystyrene (PS) in powder form.

NIR-spectra of polyamid (PA) in powder form.
NIR-spectra of polyamid (PA) in powder form.
8.2 Identification of environmental plastic samples with SIMCA.

B1 sample 1, polyethylene.

B2 sample 2, polyethylene.

B1 sample 3, polyethylene.
B1 sample 4, polypropylene.

B1 sample 5, polyethylene.

B1 sample 6, polypropylene.
B1 sample 7, unidentified.

B1 sample 8, polyethylene.

B1 sample 9, unidentified, possibly polyethylene.
B1 sample 9 unidentified, possibly polyethylene.

B1 sample 10, polypropylene.

B1 sample 11, polyethylene.
B1 sample 12, polyethylene.

B2 sample 1, polyethylene.

B2 sample 2, polyethylene.
B2 sample 3, polypropylene.

B2 sample 4, polypropylene.

B2 sample 5, polyethylene.

B2 sample 6, unidentified.
B2 sample 7, polyethylene.

B2 sample 8, polyethylene.
B2 sample 9, polyethylene.

B2 sample 10, polypropylene.

B2 sample 11, polyethylene.
B2 sample 12, polyethylene.

B3 sample 1, polyethylene.

B3 sample 2, polyethylene.
B3 sample 3, unidentified

B3 sample 4, polyethylene.

B3 sample 5, polypropylene
B3 sample 6, polyethylene.

B3 sample 7, polystyrene.

B3 sample 7, polystyrene.
B3 sample 8, polyethylene.

B3 sample 9, unidentified.

B3 sample 10, polypropylene.
B3 sample 11, polypropylene.

B3 sample 12, polyethylene.

B4 sample 1, unidentified.
B4 sample 2, polyamide.

B4 sample 3, polypropylene.

B4 sample 4, polyethylene.
B4 sample 5, unidentified

B4 sample 6, polyethylene.

B4 sample 7, polypropylene.
B4 sample 8, polyethylene.

B4 sample 9, unidentified.

B4 sample 10, polyethylene.
B4 sample 11, polypropylene.

B4 sample 12, polyethylene.
8.3 Sample size test

Complete list of NIR-spectra from samples with a surface area ranging from 100mm² down to 0.36mm².
sample surface area 3x2mm

sample surface area 2x2mm

sample surface area 1x1mm