RAMAN SPECTROSCOPY AND FUSION CLASSIFICATION TO IDENTIFY PLASTIC RECYCABLES TARGETING MICROPLASTICS

Beauty K. Chabuka, John H. Kalivas

Department of Chemistry, Idaho State University, 921 S. 8th Avenue, Pocatello, ID 83209, USA

chabbeau@isu.edu, kalijohn@isu.edu

Abstract

Identification of plastic type for microplastic particles (size range of 0.001 mm – 5 mm) is vital to understand the sources and consequences of microplastics in the environment. Fourier-transform infrared and Raman spectroscopy are two dominating techniques used to identify microplastics. The most common method to identify microplastics with spectroscopic data is library searching, a process that utilizes search algorithms against digital databases containing spectra of various plastics. Presented in this study is a new method to utilize spectroscopic data called fusion classification. Fusion classification consists of merging multiple non-optimized classification methods (classifiers) to assign samples into categories (classes). The purpose of this study is to demonstrate the applicability of fusion classification to identify microplastics..

Objective

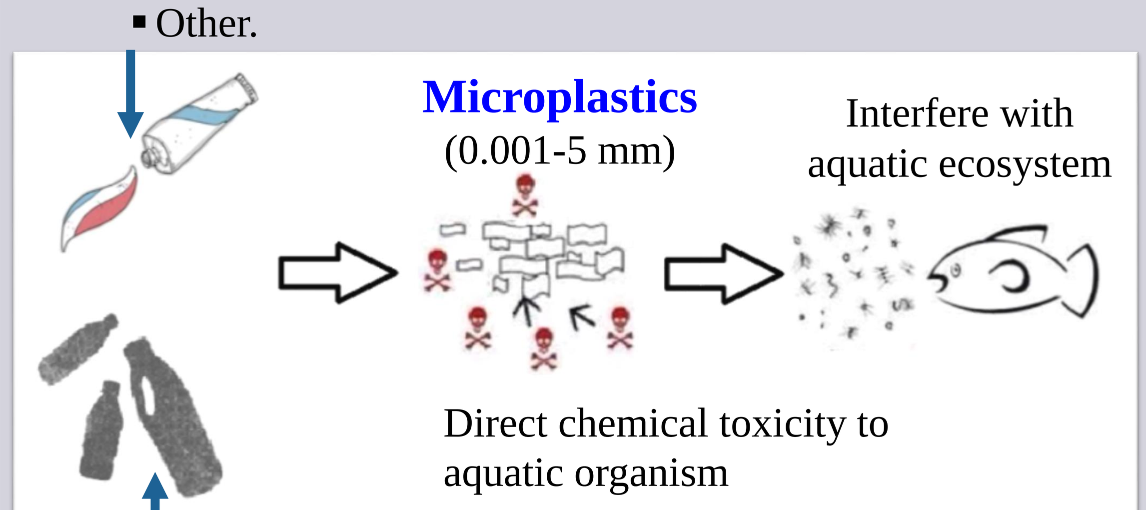
- Identify plastic recyclables using fusion classification to improve microplastic identification accuracy

Background

- > 4.5 billion metric tons of plastic produced in 2015.
- 36.2 billion metric tons projected by 2050.
- 4.8 – 12.7 million metric tons enter the ocean annually.

Primary Source

- Intentionally engineered:
  - Microbeads used in cosmetic products.
  - Other.



Secondary Source

- Consequence of:
  - Photolytic, mechanical, thermal and biological degradation of any plastic goods.

Limitations of Spectroscopic Analysis

- Interference of spectroscopic data caused by:
  - Sediments
  - Degree of degradation
  - Additives such as dyes, antioxidants, etc.

Spectroscopy

Library Matching (Common method)

Fusion Classification (New method)

Approach

Fusion Classification

- Assigning a sample to a category (class) using classification methods (classifiers).
- 17 classifier used in order to:
  - Reduce risk misidentification.
  - Improve classification accuracy.
  - Overcome limitations of stand alone classifiers.

Table 1: Classifiers

Classifiers with Tuning Parameter	Classifiers with No Tuning Parameter
▪ Mahalanobis distance (MD) ▪ Q-residual (Qres) ▪ Sine ▪ Divergence criterion (DC) ▪ Partial least squares discriminant analysis (PLS2-DA) ▪ k nearest neighbor (kNN)	▪ Euclidean distance ▪ Procrustes analysis unconstrained (PA) ▪ Inner product correlation ▪ Determinant ▪ Procrustes Analysis constrained (PA[a]) ▪ Cosine ▪ Extended inverted signal correction difference (EISCD)

Classifiers with Tuning Parameter

- Tuning parameter based on a number value:
  - PLSDA - latent variables (LVs)
  - kNN - number of nearest neighbors
  - MD, Qres, DC, and Sine – eigenvectors

Classifiers with No Tuning Parameter

- Determine the degree of similarity for a target sample compared to each class mean.
- Threshold selection required.

Our Method

- No training (optimization) , weights, or threshold selection of each classifier:
  - Uses raw values.
- Optimization based on a window of respective tuning parameter values:
  - Simplifies classification ensemble

Tuning Parameter Window Selection

- Rule of thumb;
  - 99% information of class (**X**) is captured.
  - LVs and eigenvectors are not excessively composed of noise.
  - Maximum window size is based on the rank (k) of smallest class

Example: Eigenvector based single classifier. Where k is the rank of the smallest class.

1 Eigenvector	1—2 Eigenvector	1—3 Eigenvector	....	1— k Eigenvector

1st Window

2nd Window

kth Window

Brett Brownfield, Tony Lemos, and John H. Kalivas *Analytical Chemistry* **2018** *90* (7), 4429-4437

Fusion Rule: SUM

- Values normalized to unit length.
- Samples assigned to class with lowest sum.

Classifier

- 1—5 PlS2-DA
- 6—10 kNN
- 11— 5 MD
- 16—20 Sinθ
- 21—25 Q-res
- 26—30 DC
- 30 — 41 Non-traditional classifiers

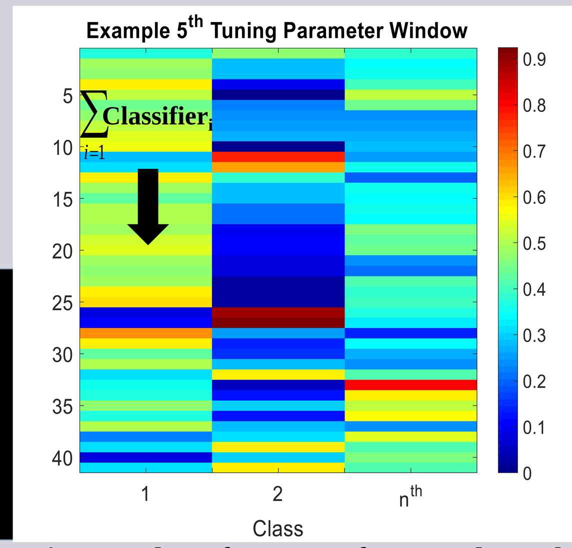


Fig. 1: Classification of a sample at the 5th tuning parameter window

% Performance Parameters

	Belong to Class	*Does not belong to Class*
Positive Result	**True Positive (TP)**	**False Positive (FP)**
Negative Result	**False Negative (FN)**	**True Negative (TN)**

$$\%Accuracy = \frac{TP+TN}{TP+TN+FP+FN} \times 100$$

$$\%Sensitivity = \frac{TP}{TP+FN} \times 100$$

$$\%Specificity = \frac{TN}{TN+FP} \times 100$$

Experimental Design

Table 2: Sample information breakdown103 samples and 188

Class #	Plastic Types	# of Samples	# of Spectra
1	Polyethylene Terephthalate (PET)	28	40
2	High density polyethylene (HDPE)	23	38
3	Polyvinyl chloride (PVC)	4	17
4	Low density polyethylene (LDPE)	18	28
5	Polypropylene (PP)	11	28
6	Polystyrene (PS)	19	37

Allen, V., Kalivas, J. H., & Rodriguez, R. G. (1999). Post-Consumer Plastic Identification Using Raman Spectroscopy. *Applied Spectroscopy, 53*(6), 672-681.

Data Sets

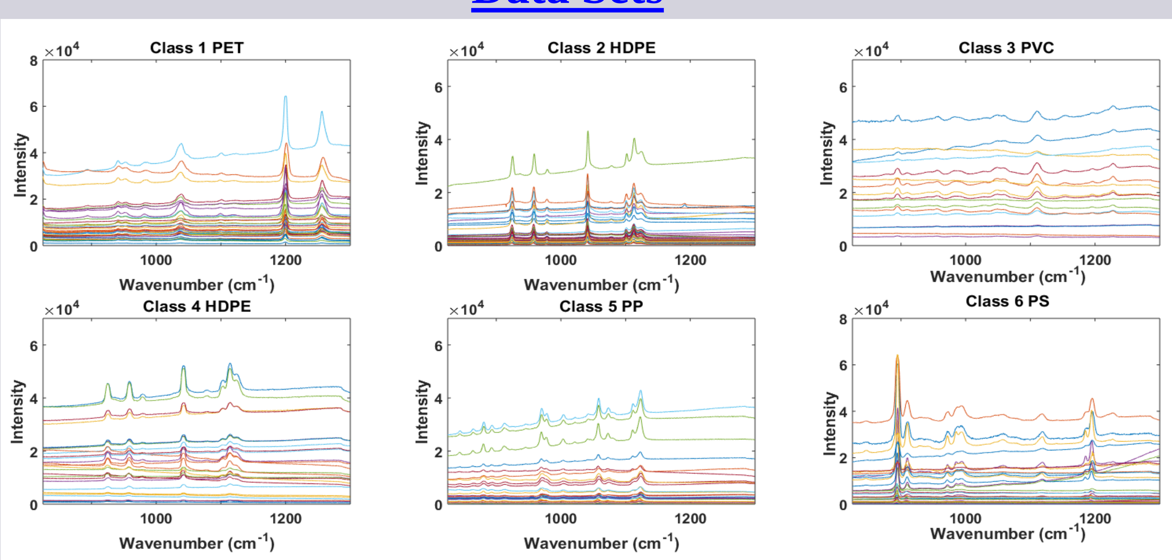


Fig. 2: Raman spectral data for each plastic type i.e. PET, HDPE, PVC, HDPE, PP and PS.

Results

Table 3: Overall (188) library matching results

% Performance Parameter	No Threshold	Threshold Cos θ ≥ 0.70	0.75	0.85	0.90
Accuracy	96.3	92.3	89.9	58.7	0
Sensitivity	96.4	85.8	81.7	41.6	0
Specificity	50	100	100	100	0

- Comparing fusion to frequently used stand alone classifiers

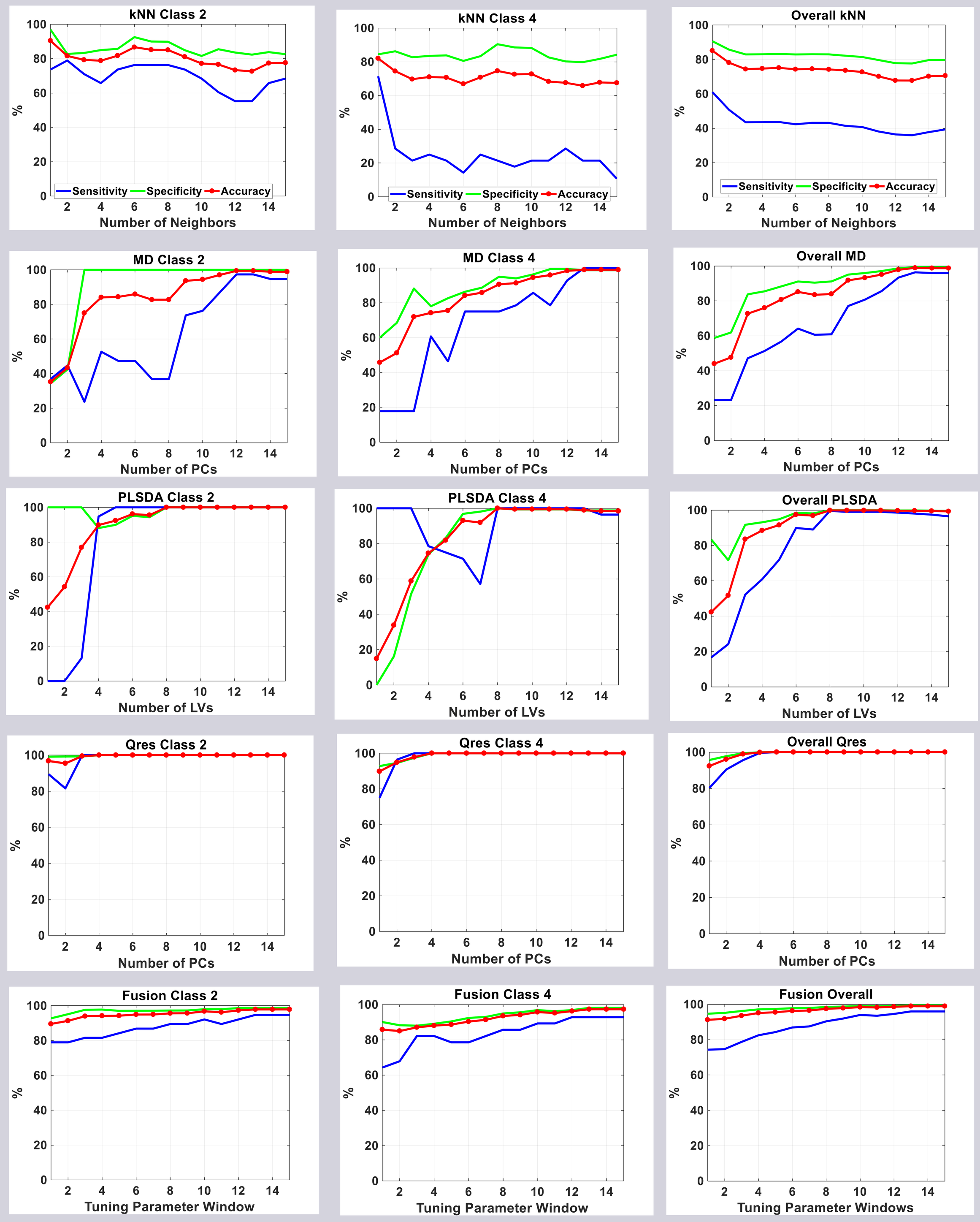


Fig.2: Each figure shows accuracy (red), sensitivity (blue) and specificity (green)

Conclusion

Library Matching	Fusion Classification
▪ Threshold selection: ▪ Value is subjective ▪ Too high— risk not identifying samples. ▪ Too low— risk misidentification of samples.	▪ No threshold selection for individual classifiers: ▪ Simplifies classification. ▪ Window size is used instead based on; ▪ Class with lowest rank. ▪ Higher accuracy, sensitivity and specificity than standalone classifiers: ▪ Reduces the risk of misclassifying abnormal samples. ▪ Identification is based on available classes.

Future Work

- Apply fusion classification to identify;
  - Physically degraded colored microplastic using Micro-Raman and Micro-FTIR.
  - Microplastic particles in the Snake river

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