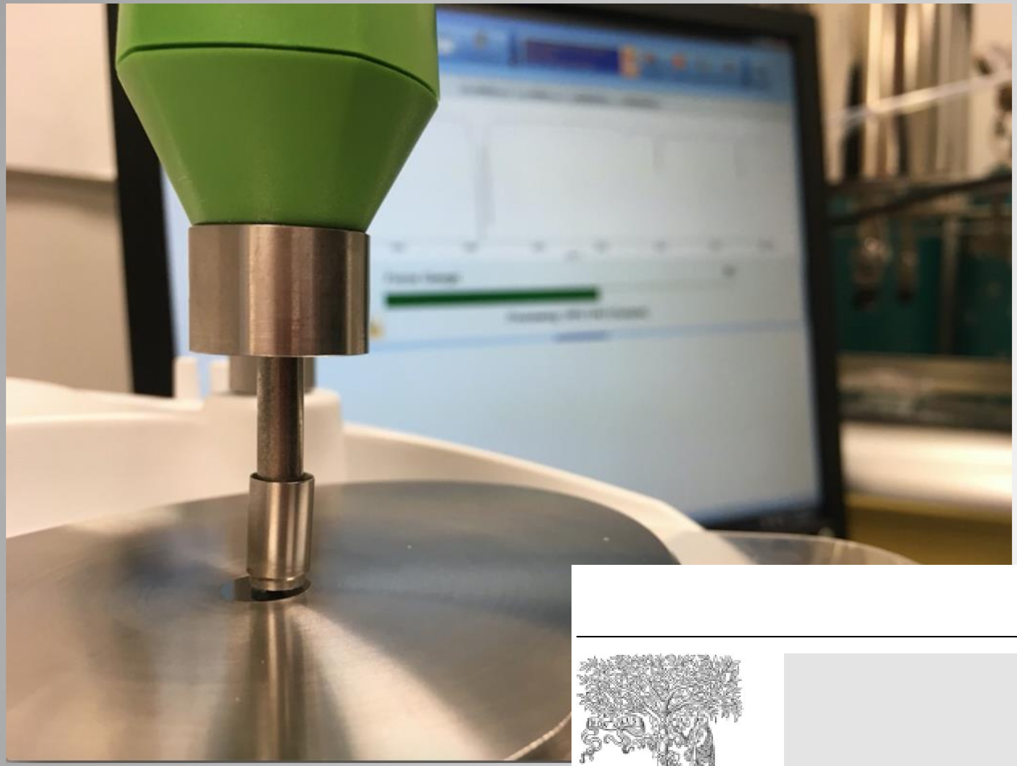
Validation of ATR FT-IR to identify polymers of ingested plastic marine debris



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Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms

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NOAA FISHERIES
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

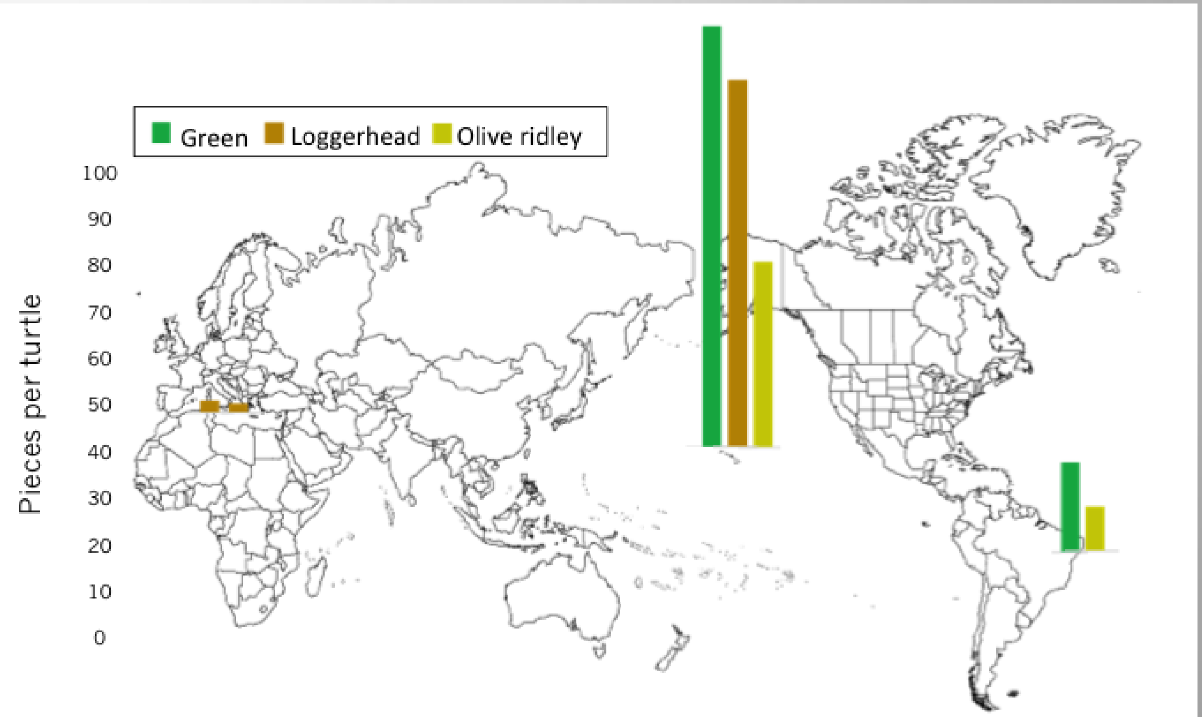
USGS
science for a changing world

UNIVERSITY OF HAWAIʻI

Ingestion of Marine Plastic Debris

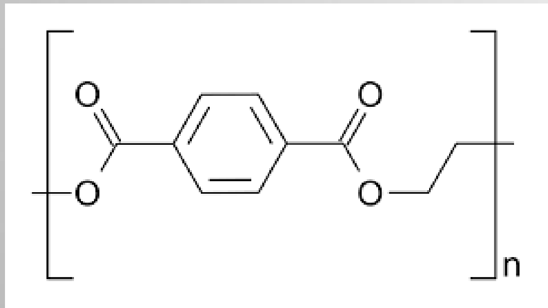
- 223 species of sea birds, sea turtles, and marine mammals have been documented to ingest plastic (Kuhn et al., 2015)
- Pacific pelagic-phase sea turtles ingest far more than sea turtles elsewhere (Clukey et al., 2017)

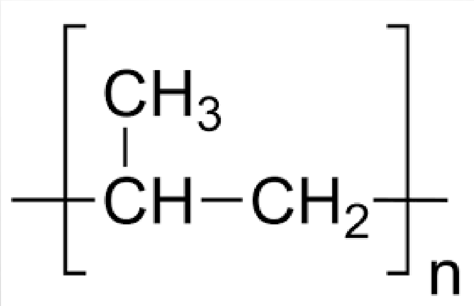
www.http://plasticos.se

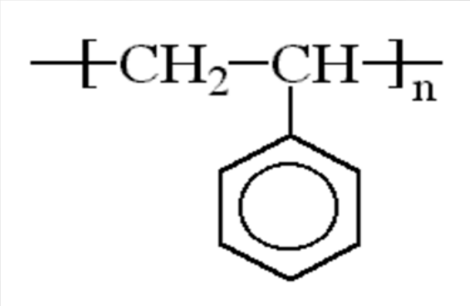


Plastic Polymers

www.albertaplasticsrecycling.com







-Each polymer type has a unique density range that affects its distribution in the water column

Why Identify Polymers?

-Know which ones are most prevalent

-Understand transport and fate in the ocean (maybe source)

-Predict sorption of organic pollutants
(Rochman et al., 2013)

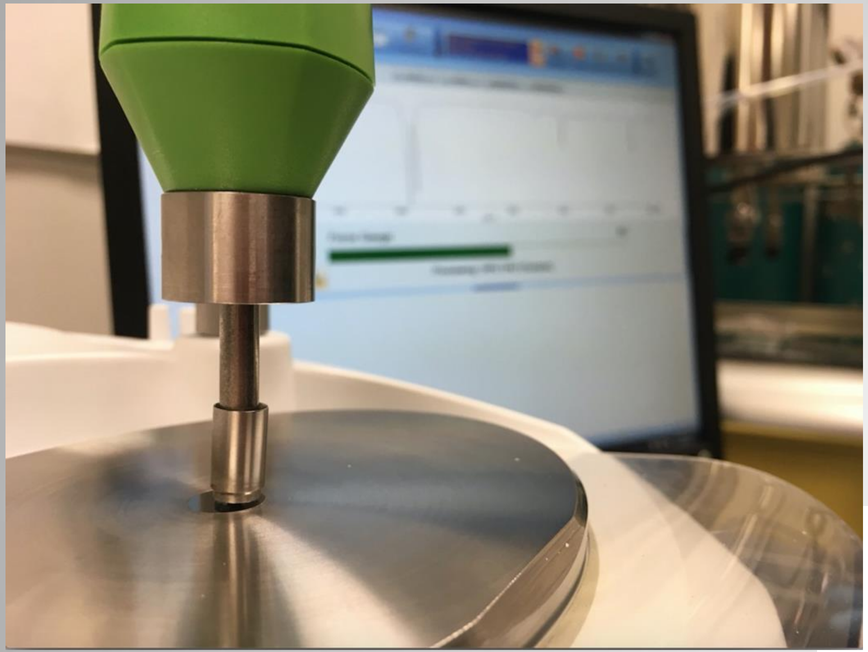
-Inform regulations on production, use, and disposal

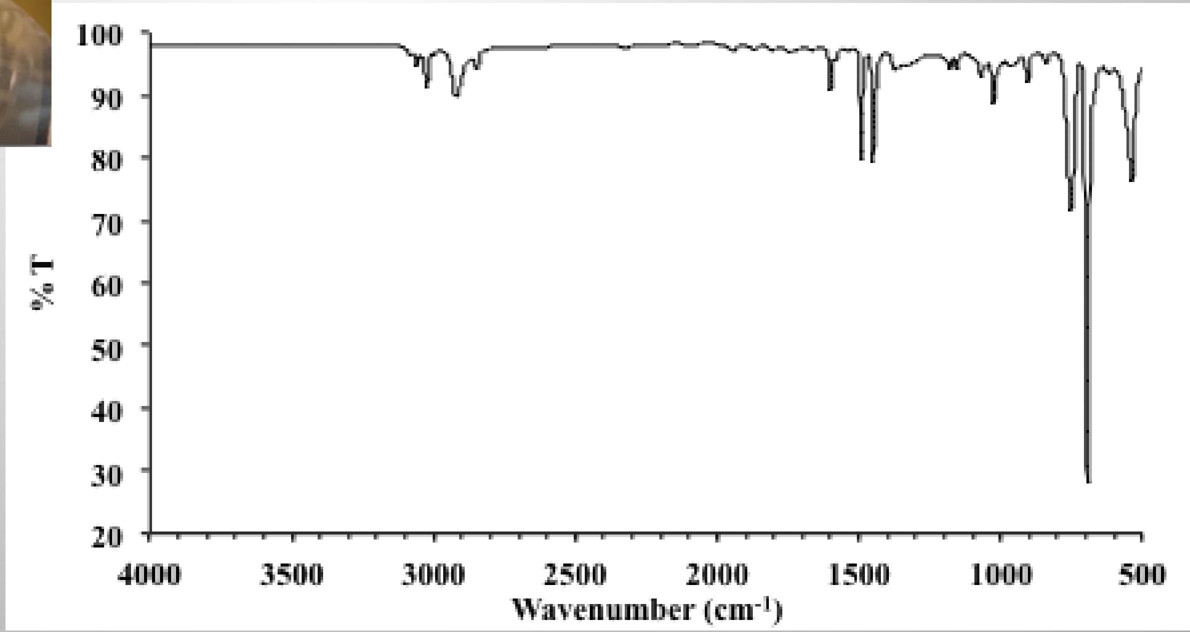
-Monitor effectiveness of management
- -Recycling programs
- -Bans on specific items

www.recylclereminders.com

ATR FT-IR Analysis

-Attenuated total reflectance Fourier infrared spectroscopy





Objectives

-Can we identify weathered and digested polymers (manufactured with additives) with certainty?

Vs.

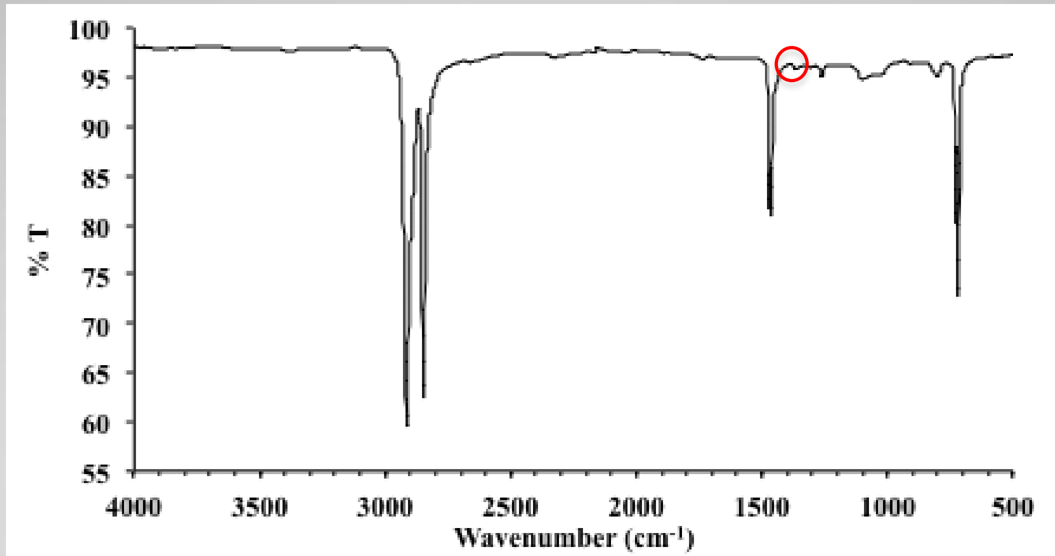
Plastic Ingested by Sea Turtles

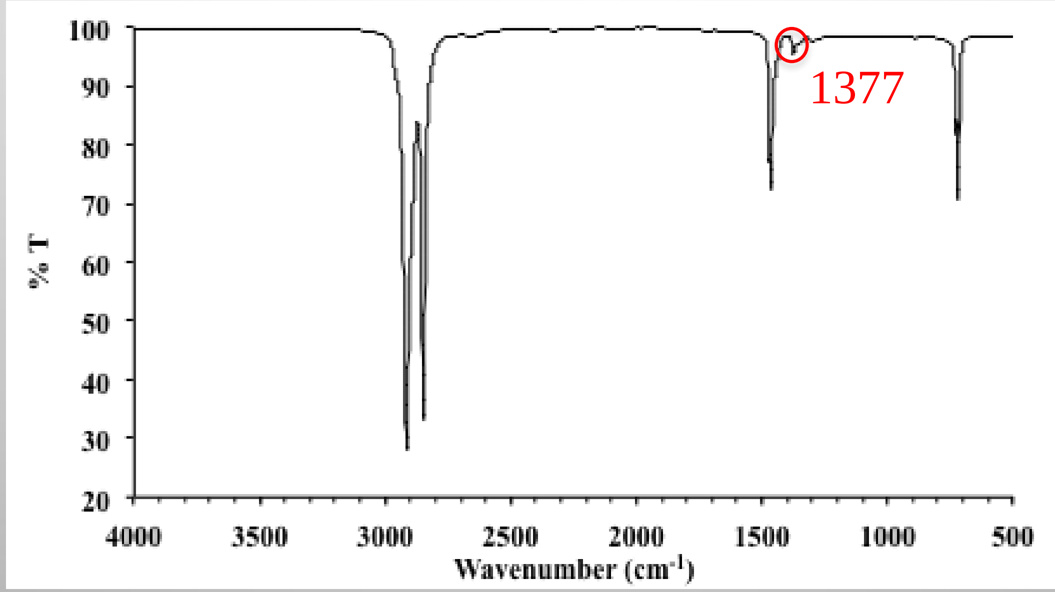
-From gut of one loggerhead sea turtle in central Pacific Ocean:

Clukey et al., 2017

Objectives

-Can we distinguish HDPE (resin #2) from LDPE (#4) with certainty?





Band at 1377?

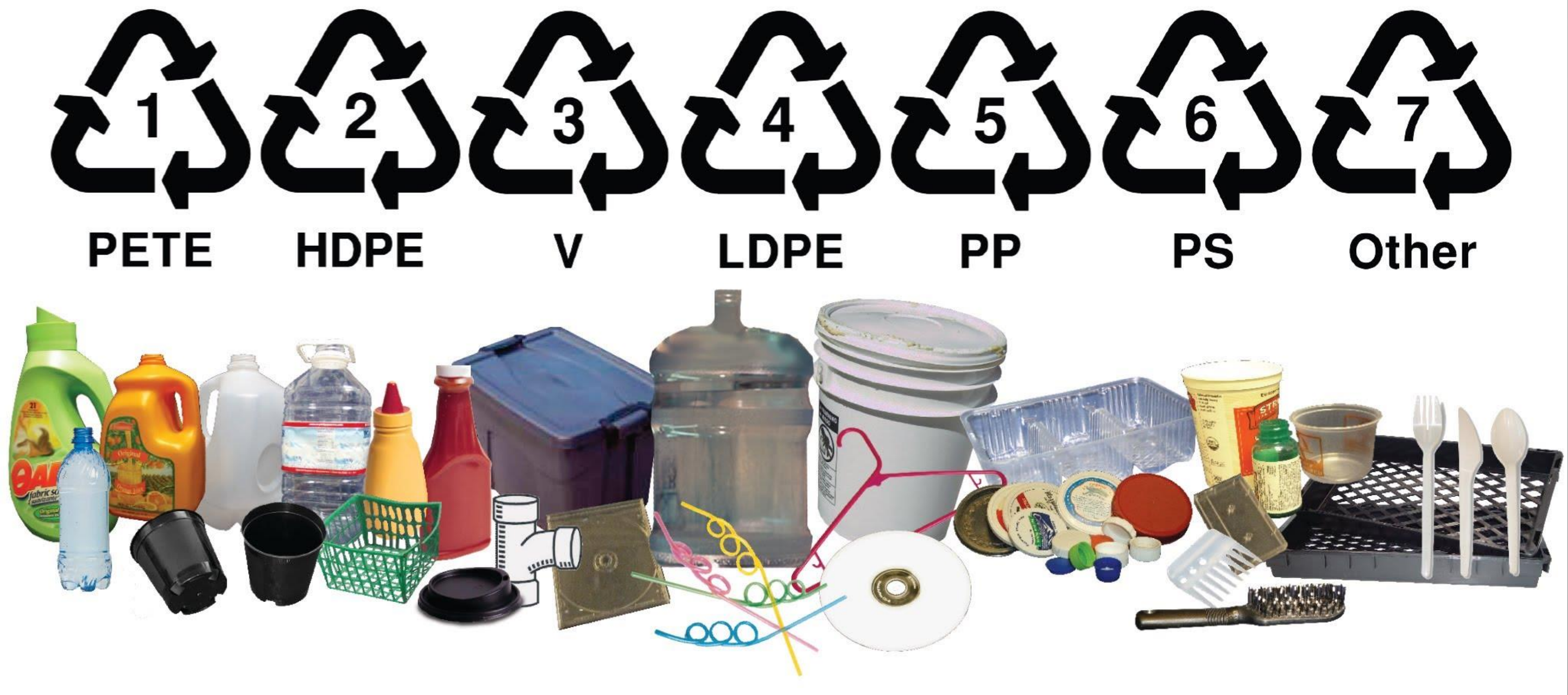
Yes = LDPE

No = HDPE

Nishikida and Coates, 2003

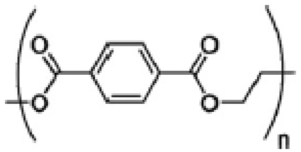
Methods

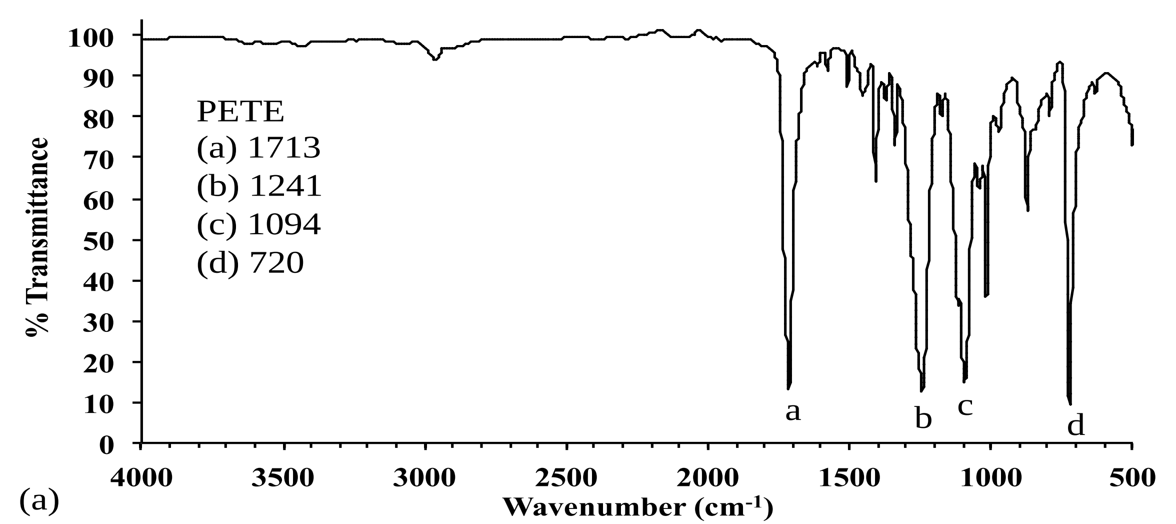
- Collected triplicate consumer goods marked with each polymer type
    - Created an FT-IR spectral library
    - Performed a blind test of 11 items by 3 students



Results: Spectral library

Table 1
List of important vibration modes and mode assignments for the ATR FT-IR spectra of eight of 16 polymers identified. The remaining eight polymers are in Table 2. Absorption bands listed are representative of vibrations critical for polymer identification. Please consult references for full lists of absorption bands.

Polymer	Resin code	Chemical structure	Absorption bands (cm^{-1}) used for identification[a]	Assignment	Reference in addition to this study
Polyethylene terephthalate (PETE)	1		1713 (a) 1241 (b) 1094 (c) 720 (d)	C=O stretch C–O stretch C–O stretch Aromatic CH out-of-plane bend	Asensio et al., 2009; Verleye et al., 2001; Noda et al., 2007



PETE
HDPE
PVC
LDPE
PP
PS
ABS
CA

EVA
Latex
Nitrile
Nylon
PC
PMMA
PTFE
FEP
PU

Jung et al., 2018
- Table 1 & Fig 1
- Offer a simple guide
- Compile absorption bands from 10 citations for 17 common polymers

Results: Blind test

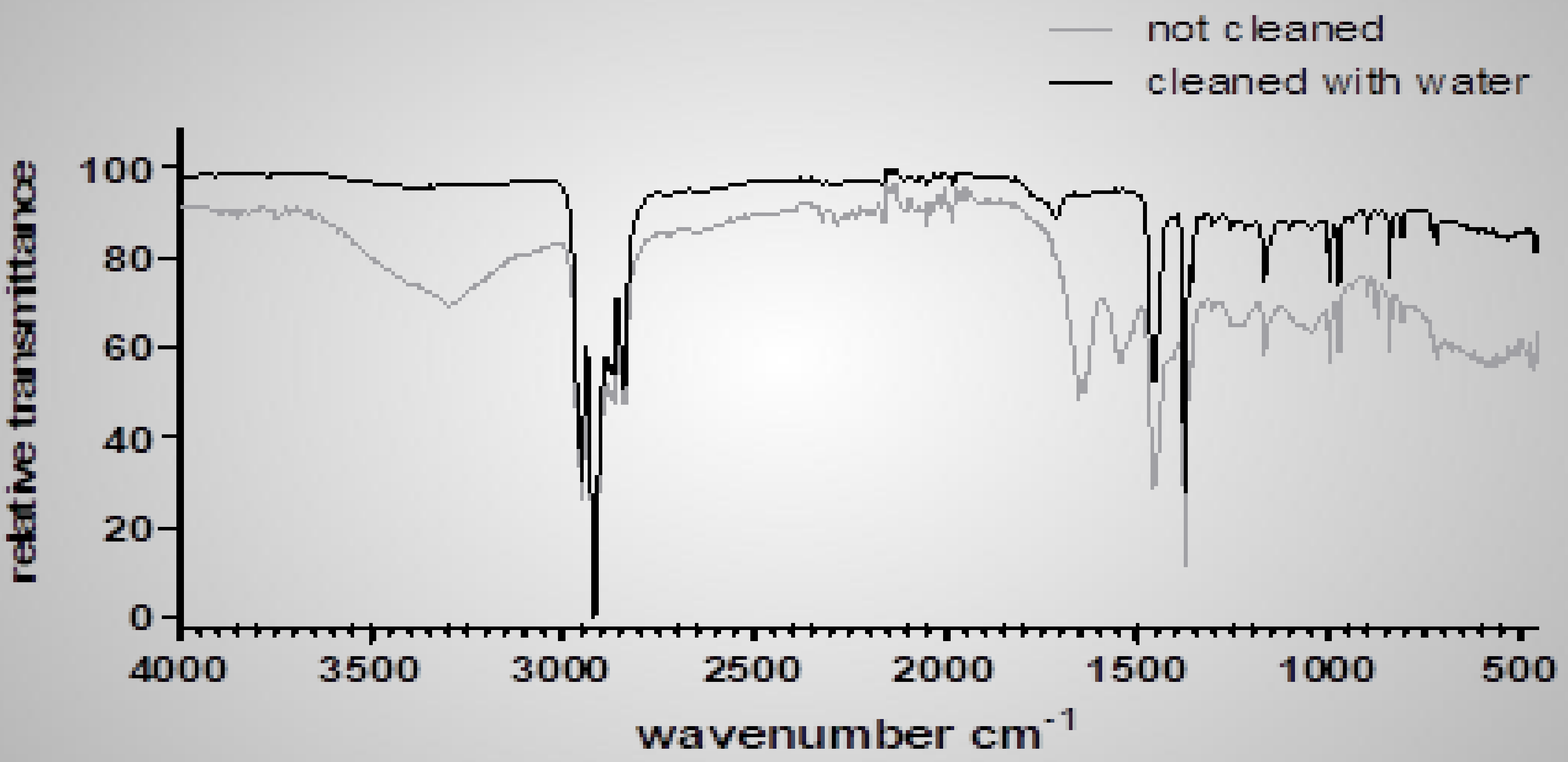
Known polymer	**Analyst 1**	**Analyst 2**	**Analyst 3**
PETE	✓ PETE	✓ PETE	✓ PETE
PETE	✓ PETE	✓ PETE	✓ PETE
HDPE	✓ HDPE	✓ HDPE	✓ HDPE
HDPE	✓ PE unknown	✓ PE unknown	✓ PE unknown
HDPE	✓ PE unknown	✓ PE unknown	✓ PE unknown
LDPE	✓ LDPE	✓ LDPE	✓ LDPE
LDPE	✓ PE unknown	✓ PE unknown	✓ PE unknown
PE unknown	✓ LDPE	✓ LDPE	✓ LDPE
PP	✓ PP	✓ PP	✓ PP
PP	✓ PP	✓ PP	✓ PP
PS	✓ PS	✓ PS	✓ PS
Score	**100%**	**100%**	**100%**
HD vs LD	**50%**	**50%**	**50%**

Methods

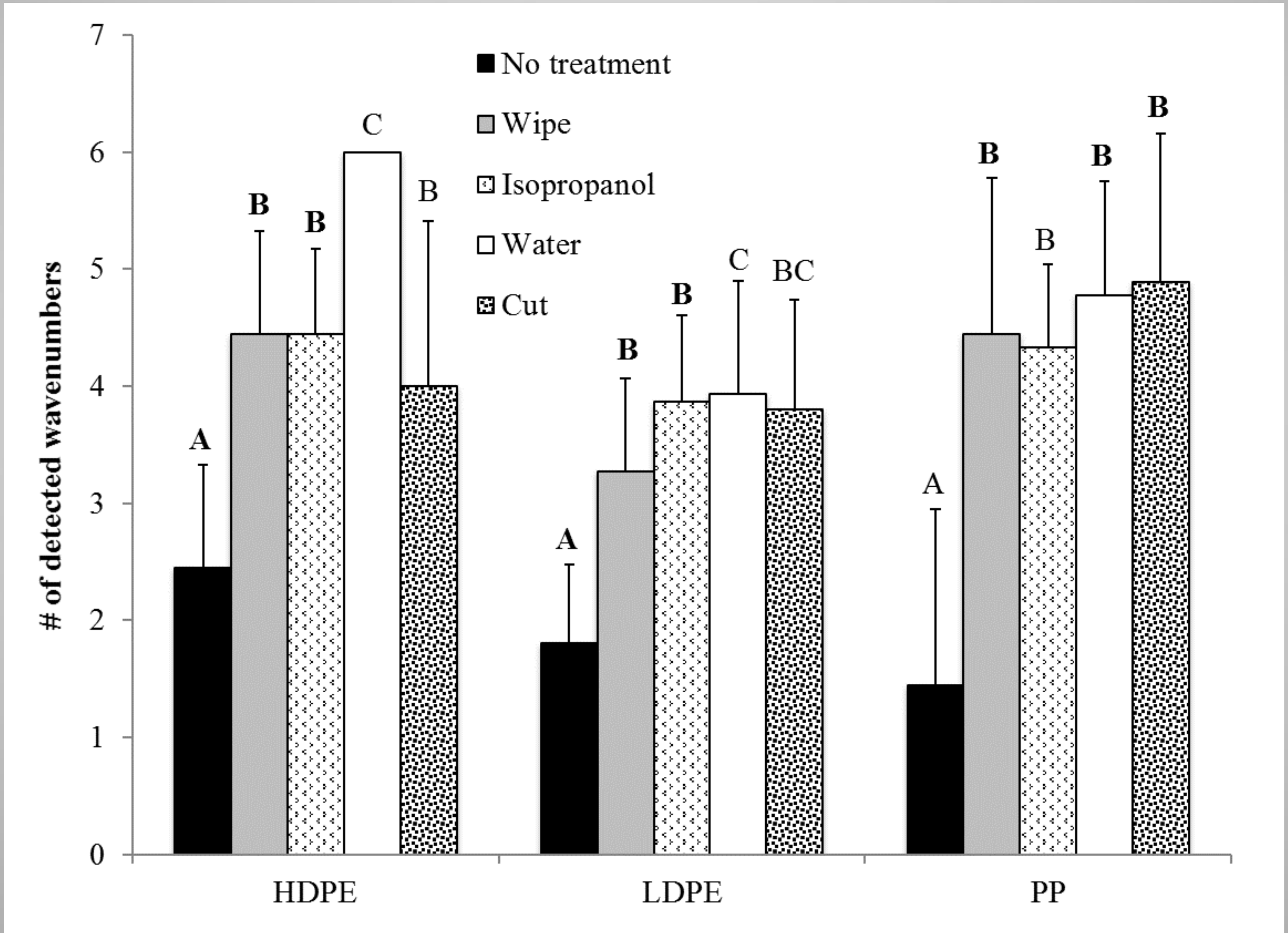
-Assessed plastic debris from sea turtle gastrointestinal tracts

- Tested 5 cleaning methods on 3 different polymers
- Performed inter-laboratory comparison
  - FT-IR vs. HT-SEC with multiple detectors (n=17)

Results: Cleaning Methods



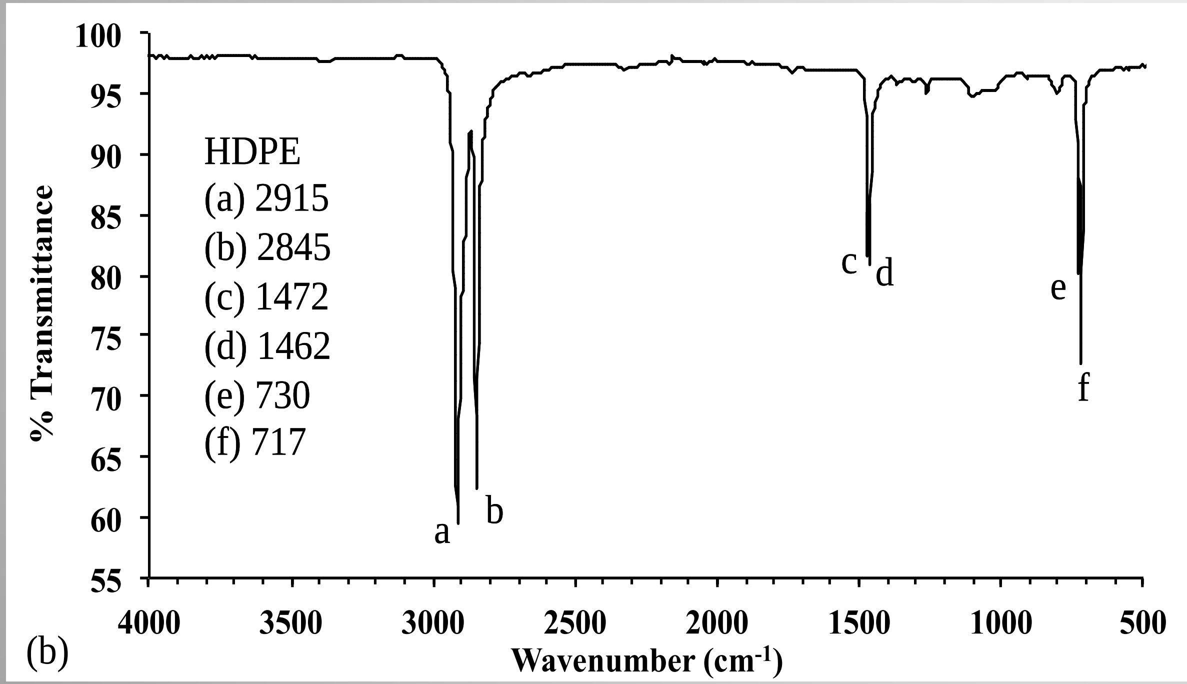
Results: Cleaning Methods



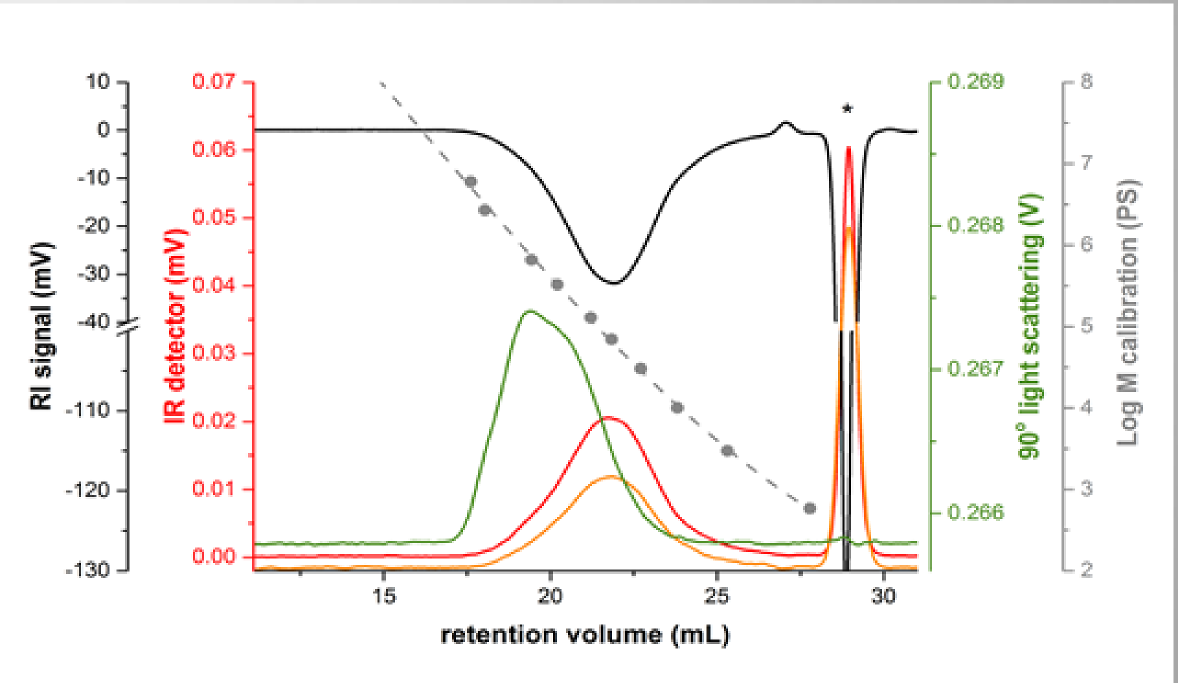
Results: Inter-laboratory comparison

HDPE:

FT-IR spectrum



HT-SEC



Results: FT-IR vs HT-SEC

94% matched

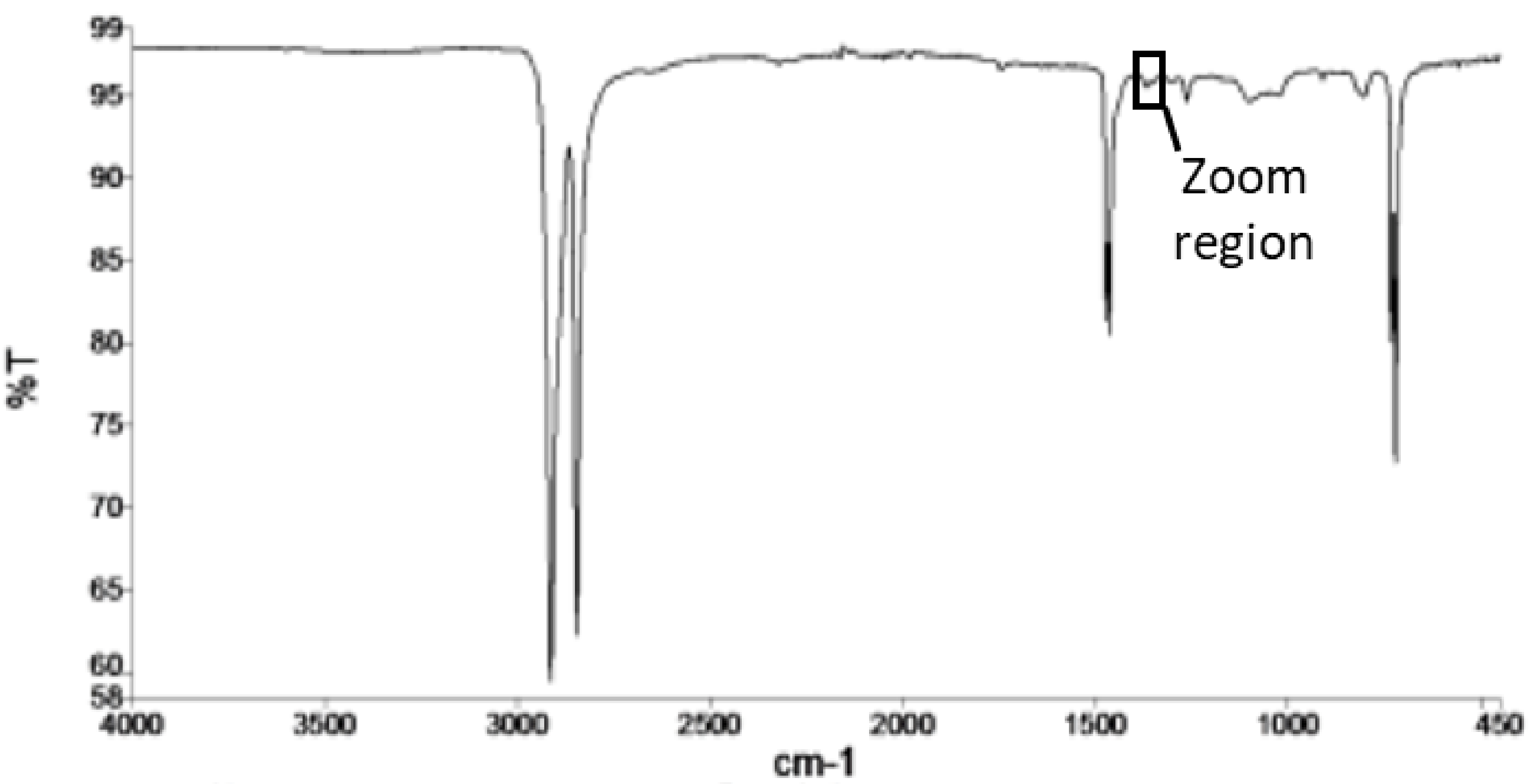
100% LD vs HD correct

			HT-SEC Results			
Identification by FT-IR		Identification by HT-SEC	RI peak magnitude	Average CH_3/ 1000 total C	M_n (kg/mol)	M_w (kg/mol)
PETE	✗	PU*				
HDPE	✓	HDPE	-	11.2 ± 7	1.1	36.2
HDPE	✓	HDPE	-	10.6 ± 8	26.6	161.2
HDPE	✓	HDPE	-	6.2 ± 9	6.0	83.8
HDPE	✓	HDPE	-	9.9 ± 15	5.0	32.8
HDPE	✓	HDPE	-	5.7 ± 9	15.2	80.4
LDPE	✓	LDPE	-	24.0 ± 5	42.5	148.3
LDPE	✓	LDPE	-	35.8 ± 17	0.9	70.9
LDPE	✓	LDPE	-	48.3 ± 16	2.5	65.6
LDPE	✓	LDPE	-	25.7 ± 9	32	148.4
LDPE	✓	LDPE	-	54.7 ± 12	33.2	197.1
PP	✓	PP	-	338.7 ± 6	42.4	196.4
PP	✓	PP	-	348.4 ± 18	4.7	58.6
PP	✓	PP	-	303.5 ± 5	6.8	44.5
PS	✓	PS	+	15.2 ± 23	21.7	52.5
PS	✓	PS	+	35.2 ± 27	28.2	557.2
PS	✓	PS	+	34.1 ± 51	137.6	281.7

*XPS survey scan

Methods

-Distinguish LDPE from HDPE via FT-IR



Band at 1377?

Yes = LDPE

No = HDPE

Nishikida and Coates, 2003

Methods

Band at 1377?

No = HDPE

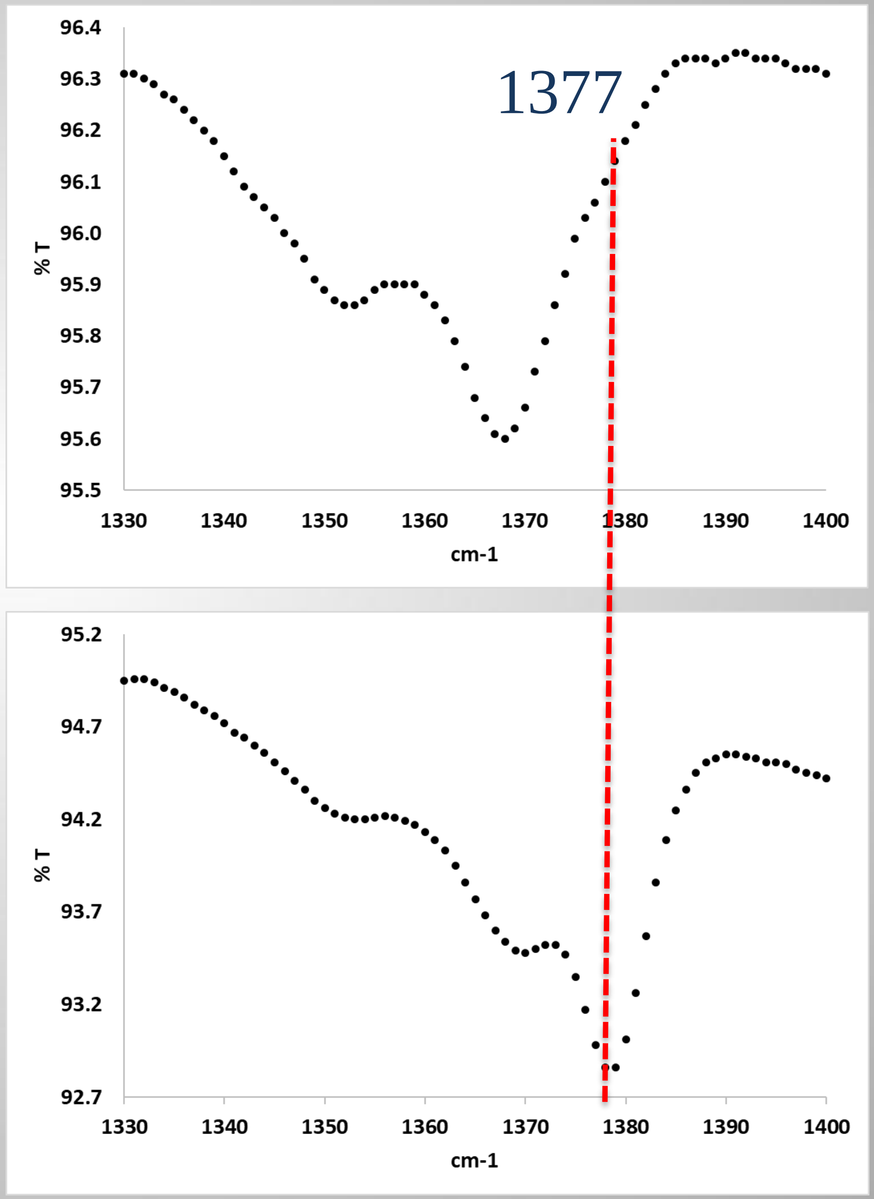
Yes = LDPE

Nishikida and Coates, 2003

70% Easy:

HDPE

LDPE



Methods

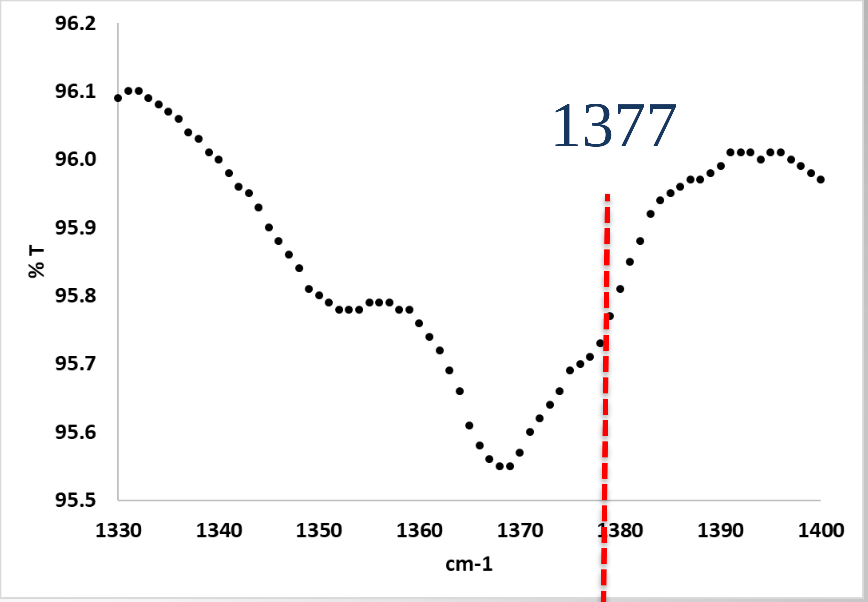
Band at 1377?

Maybe = ??

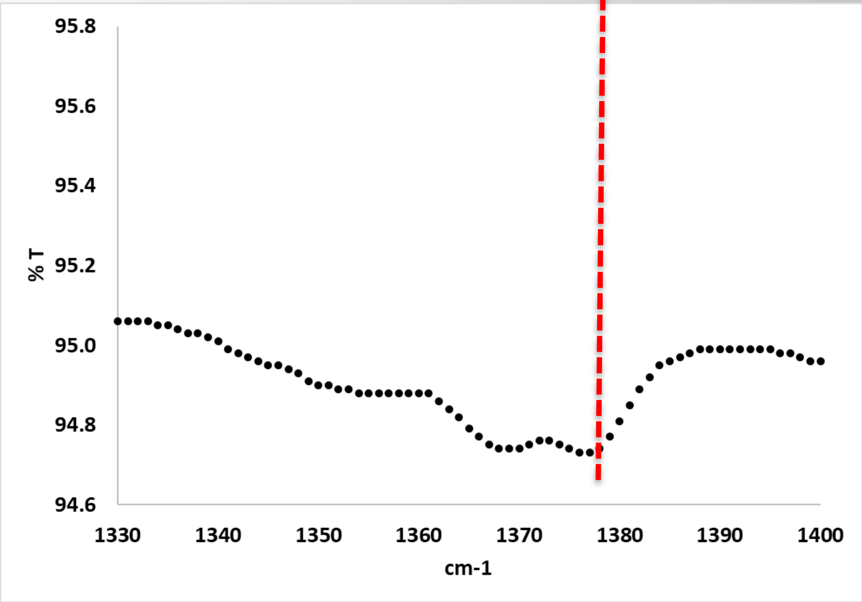
No reference

30% Not Easy:

HDPE?



LDPE?



Methods

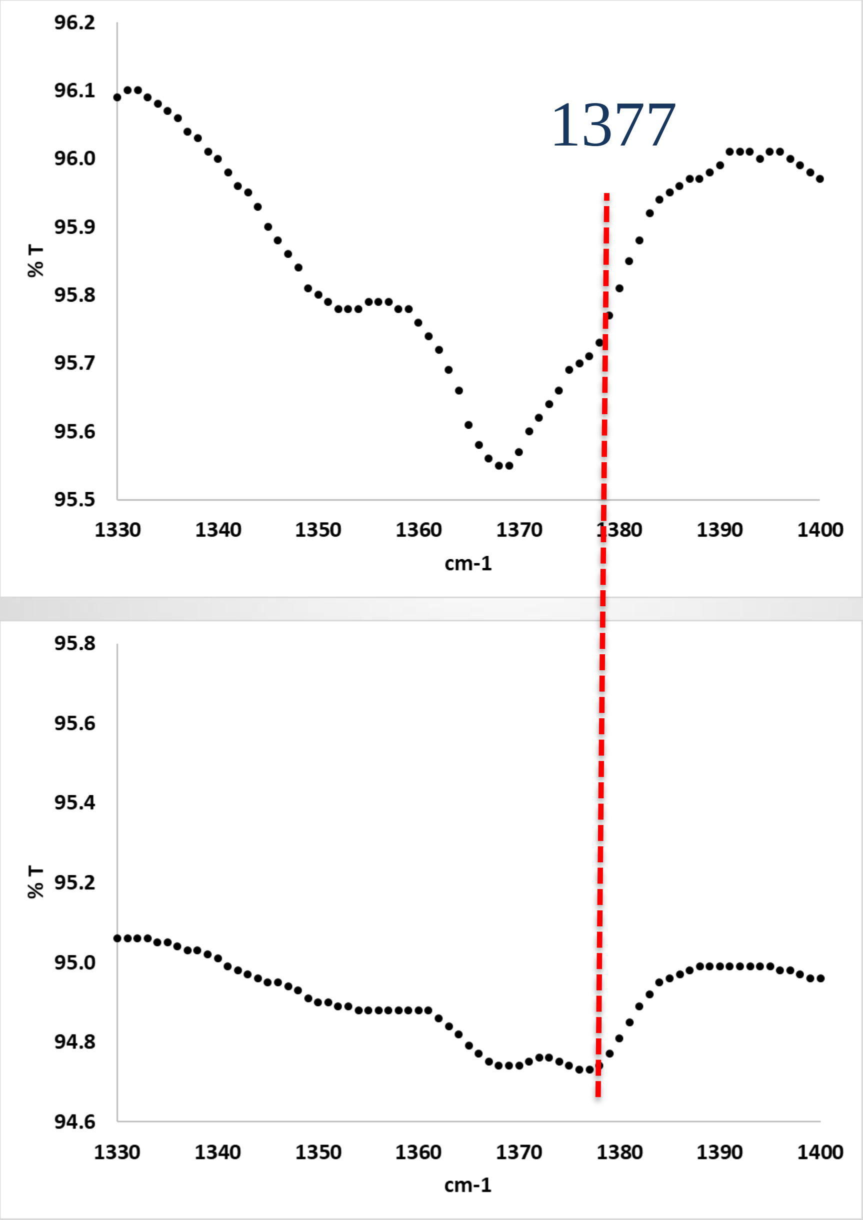
-Float-tested Hawaiian beach debris identified by FT-IR as PE (n=49)

- Assigned their spectra to “easy” or “not easy”
- Tested if they float or sink in ethanol dilutions (pivotal 0.935 g/mL)
  - LDPE float
  - HDPE sink

Results: Beach PE float test

Not Easy:

HDPE?

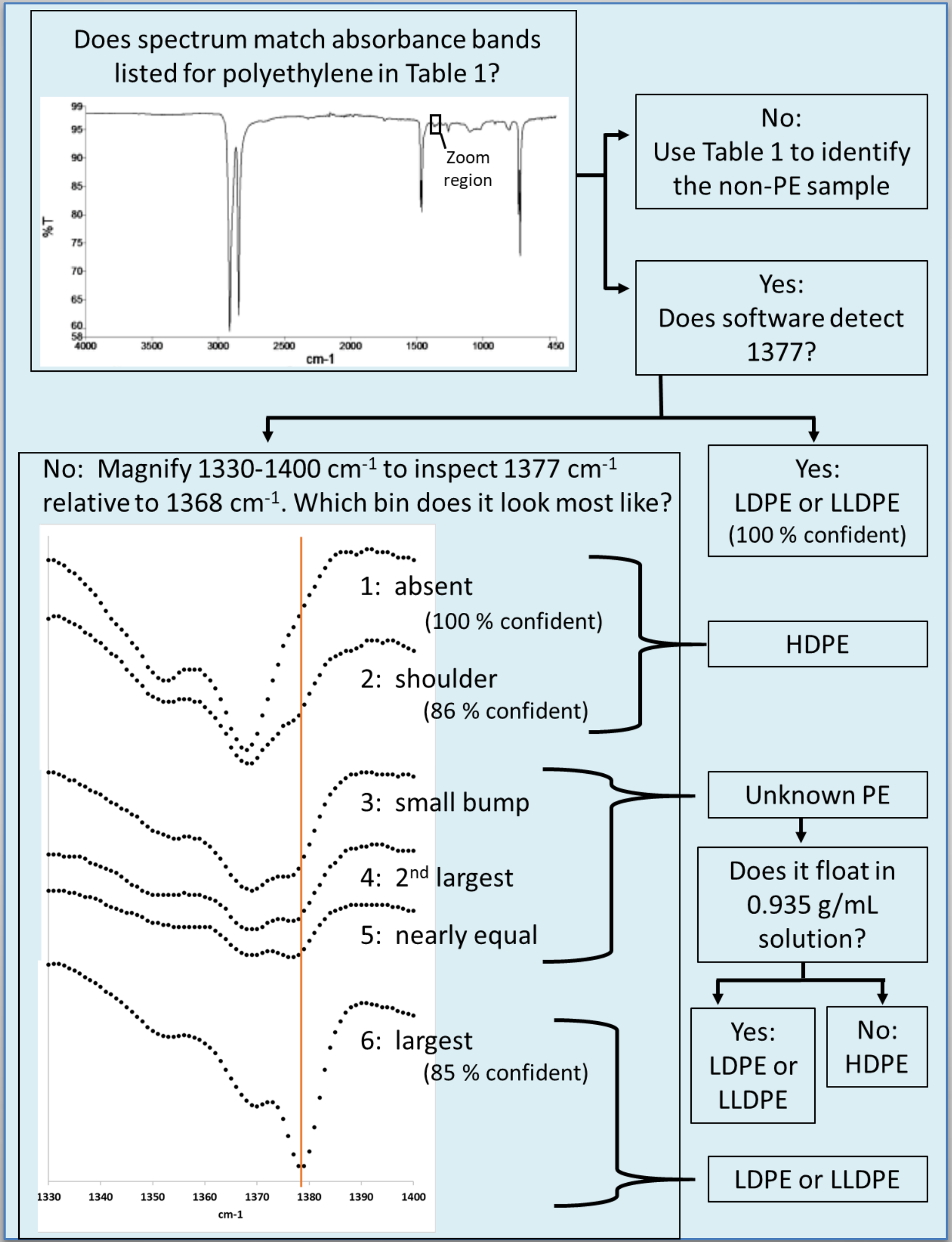


Probably.
- 12/14 sank
- 86% certainty

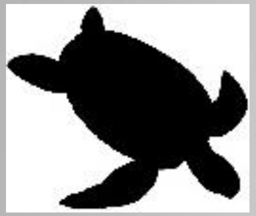
LDPE?

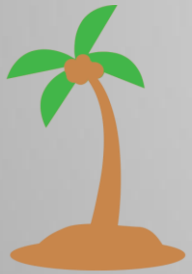
Too uncertain.
- 6/13 floated
- 46% certainty
- "unknown PE" without further testing

Results: Decision Tree



Results: Applying method





Poster	Sample Type	N	% ID by FT-IR	% of PE ID by FT-IR
116	Sea Turtle ingested debris	828	97% (99% with combo of HT-SEC)	78% (without float test)
112	Hawaiian beach debris	>4000	99%	92% (with float test)

Conclusions

- FT-IR method in Jung et al. (2018) Mar Pollut Bull 127:704-716
    - highly accurate for identifying polymers of marine debris
    - Accessible, easy-to-follow guide and decision tree for LDPE and HDPE
    - Cutting or washing with water are best cleaning methods
    - Collaborating with polymer scientists provides great benefits
    - 4 NIST SRMs were used in this study

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NIST SRMs help standardize measurements

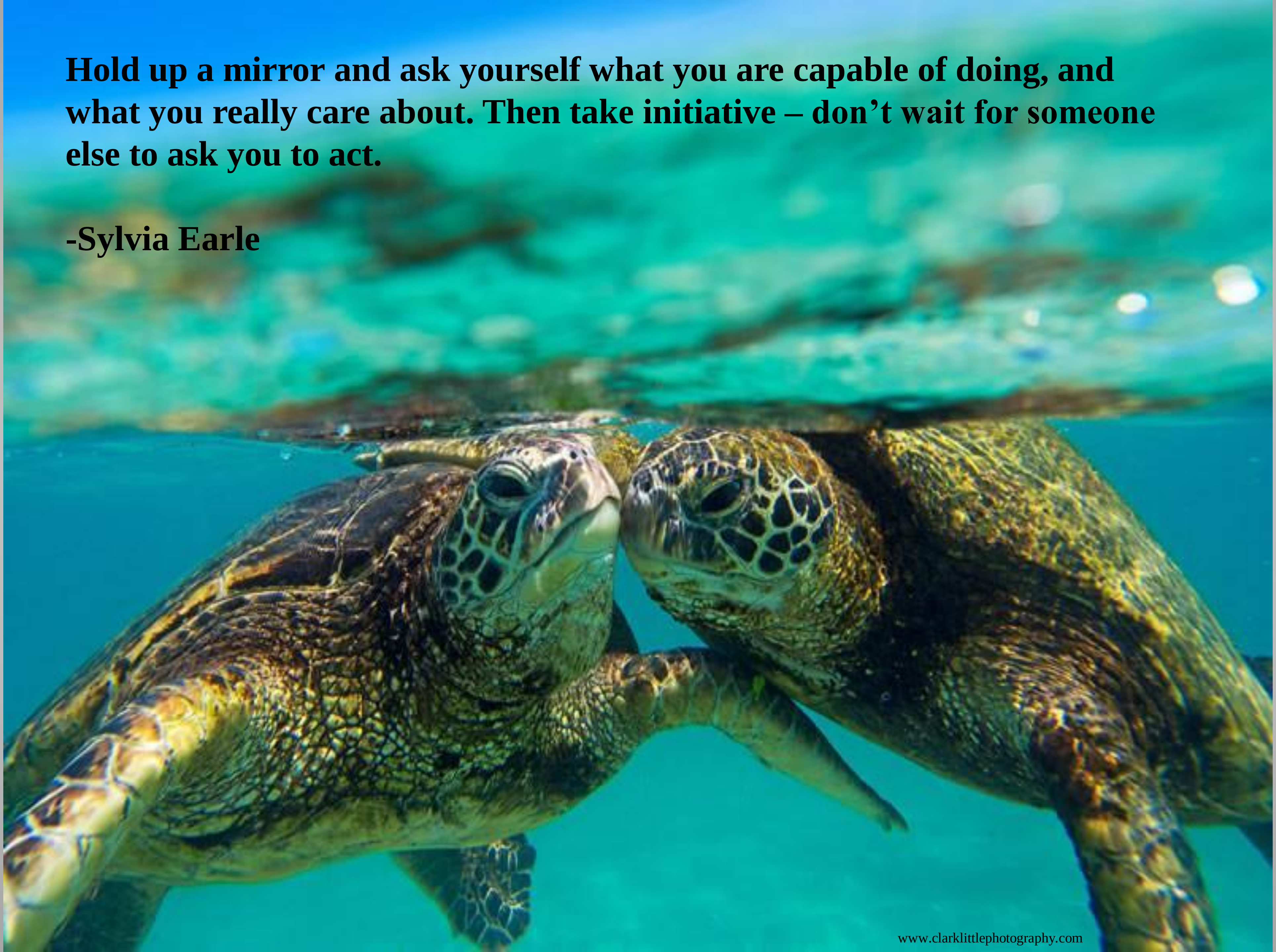
- 25 polymer SRMs available

- Are additional SRMs needed by marine debris researchers?
  - Survey: https://goo.gl/forms/nAfHzeicb82XuDir2
  - Email: Jennifer.lynch@nist.gov
  - Discuss:
    Wednesday Networking Lunch "Standard Reference Material Needs" in Garden by the Bay

Main polymer	SRM	Description
HDPE	1483a	Linear Polyethylene
HDPE	1484a	Linear Polyethylene
LDPE	1473c	Low Density Polyethylene Resin
LDPE	1476a	Branched Polyethylene Resin
PE	1474b	Polyethylene Resin
PE	1482a	Polyethylene
PE	1496	Unpigmented Polyethylene Gas Pipe Resin
PE	2855	Additive Elements in Polyethylene
PE	2885	Polyethylene (Mw, 6 280 g/mol)
PE	2887	Polyethylene (Mw, 196 400 g/mol)
PE	8540	IAEA-CH-7 (C and H Isotopes in Polyethylene Foil)
PMMA	1487	Poly(Methyl Methacrylate) (6 K Narrow Mol. Wt. Distrib.)
PMMA	1488	Poly (Methyl Methacrylate) 29 K Narrow Mol. Wt. Distrib.)
PS	705a	Polystyrene (Narrow Molecular Weight Distribution)
PS	706a	Polystyrene (Broad Molecular Mass Distribution)
PS	1453	Thermal Conductivity - Expanded Polystyrene Board
PS	1478	Polystyrene (Narrow Molecular Weight Distribution)
PS	1479	Polystyrene (Narrow Molecular Weight Distribution)
PS	1691	Polystyrene Spheres (Nominal Diameter 0.3 µm)
PS	1961	Polystyrene Spheres (30 µm Diameter)
PS	1965	Microsphere Slide (10-µm Polystyrene Spheres)
PS	2870	Relative Permittivity & Loss Tangent 1422 Cross-Linked PS
PS	2881	Polystyrene Absolute Molecular Mass Distribution Standard
PVC	2859	Restricted Elements in Polyvinyl Chloride
PVC	2861	Restricted Elements in Polyvinyl Chloride

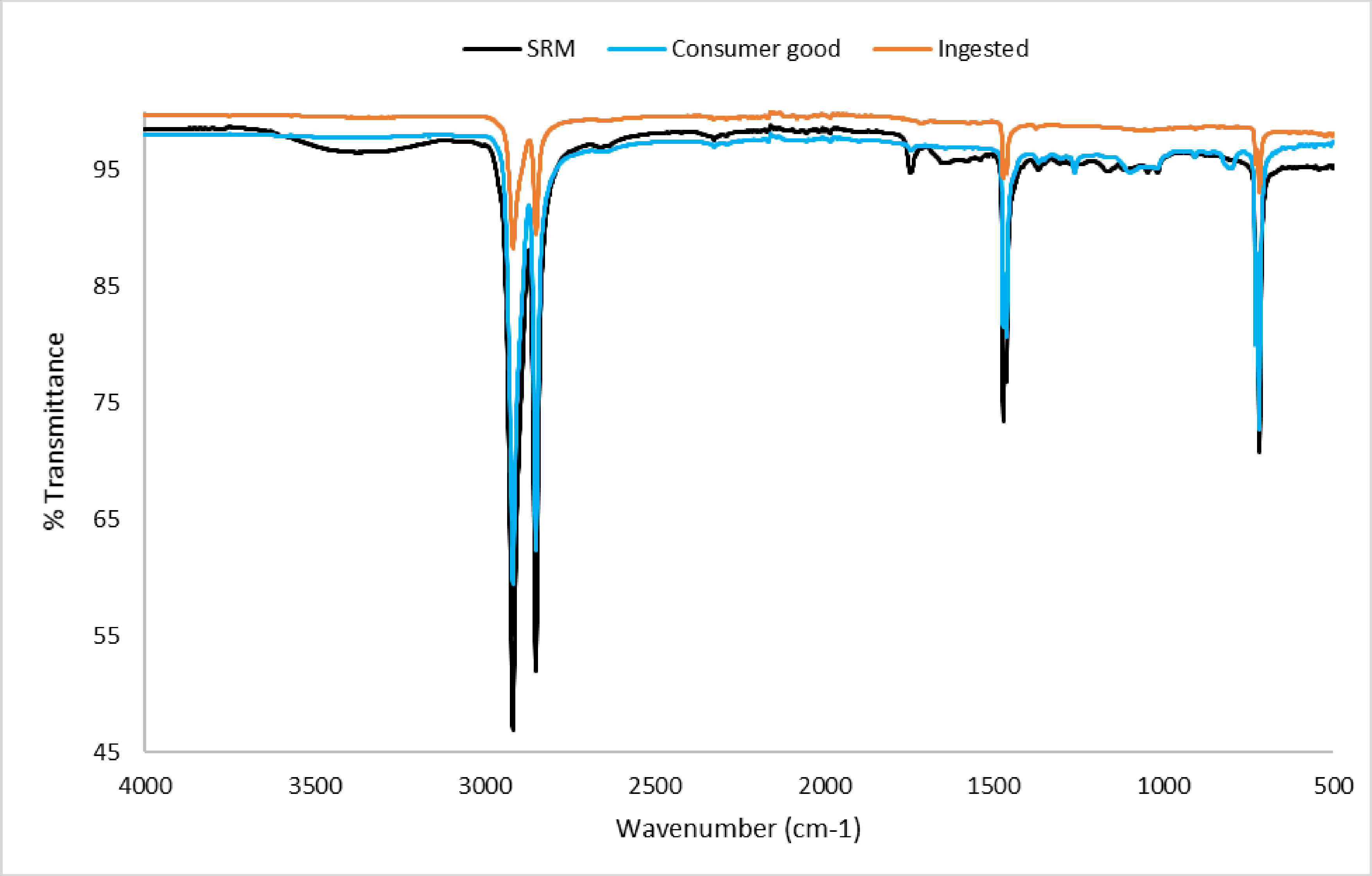
Hold up a mirror and ask yourself what you are capable of doing, and what you really care about. Then take initiative – don't wait for someone else to ask you to act.

-Sylvia Earle



www.clarklittlephotography.com

Results: Pure vs. Weathered



HDPE

Plastic Ingested by Sea Turtles

-From gut of one green sea turtle in central Pacific Ocean:

Clukey et al., 2017