HORIBA

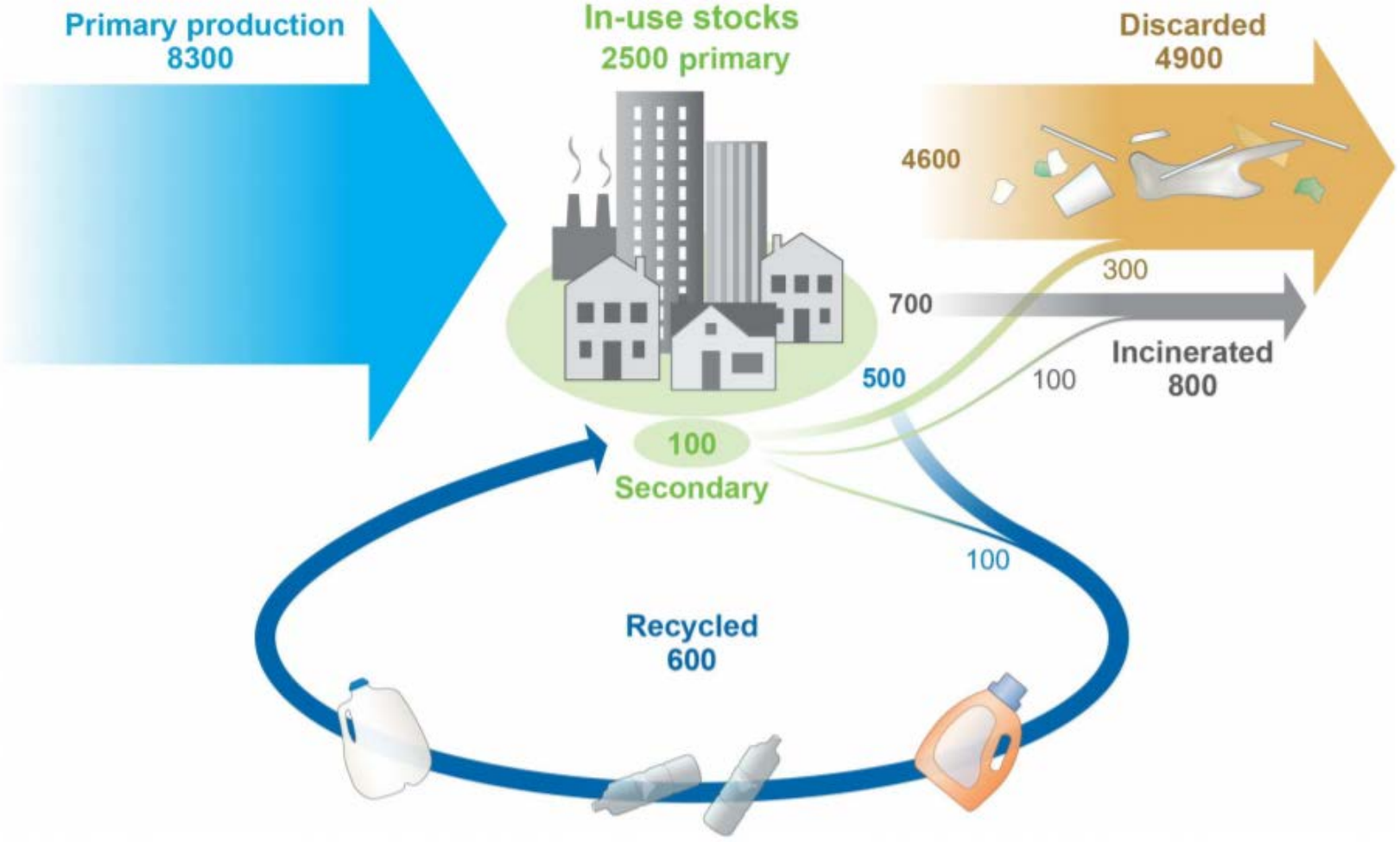
Explore the future

Impacts of Microplastics in the Urban Environment Conference
Chemical Analysis
Friday, March 29, 2019

Spectroscopic Techniques for Polymer Identification in Plastic Marine Debris

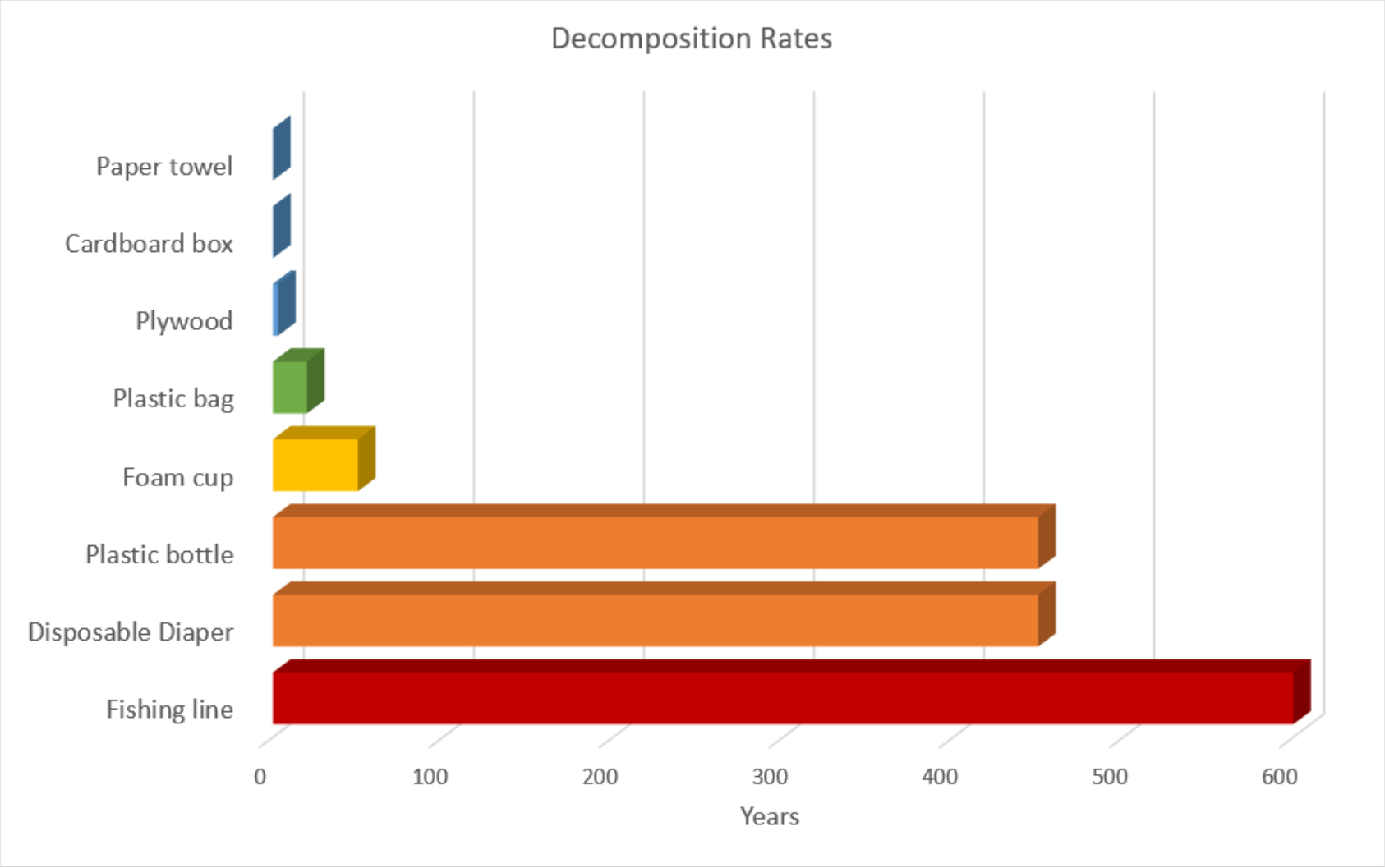
Bridget O'Donnell, Ashok Deshpande, Jennifer Lynch, Kayla Brignac, Melissa Jung, Nigel Lascelles, Dante Freeman, Davielle Drayton

Fate of Plastics



Geyer, Jambeck, Law Sci. Adv. 2017;3: e1700782

Lifetime of Plastics



Ocean Conservancy and NOAA Marine Debris

Plastic Debris in Marine Environments

- Weathering of plastics causes fragmentation
- Detrimental effect on oceans, wildlife, and potentially humans
- Evidence of plastics on coastlines, in Arctic sea ice, and on the sea surface & floor

NOAA Marine Debris Program

Techniques for Chemical Identification

Raman

Scattering technique

Sensitive to molecular vibration based on change in polarizability

No sample preparation

Susceptible to background fluorescence

Sensitive to polymer backbone structure

ATR-FTIR

Absorption technique

Sensitive to molecular vibration based on change in dipole moment

Sample mounted on diamond crystal and compressed

Susceptible to water absorption

Sensitive to polymer side chains

Pyrolysis GC-MS

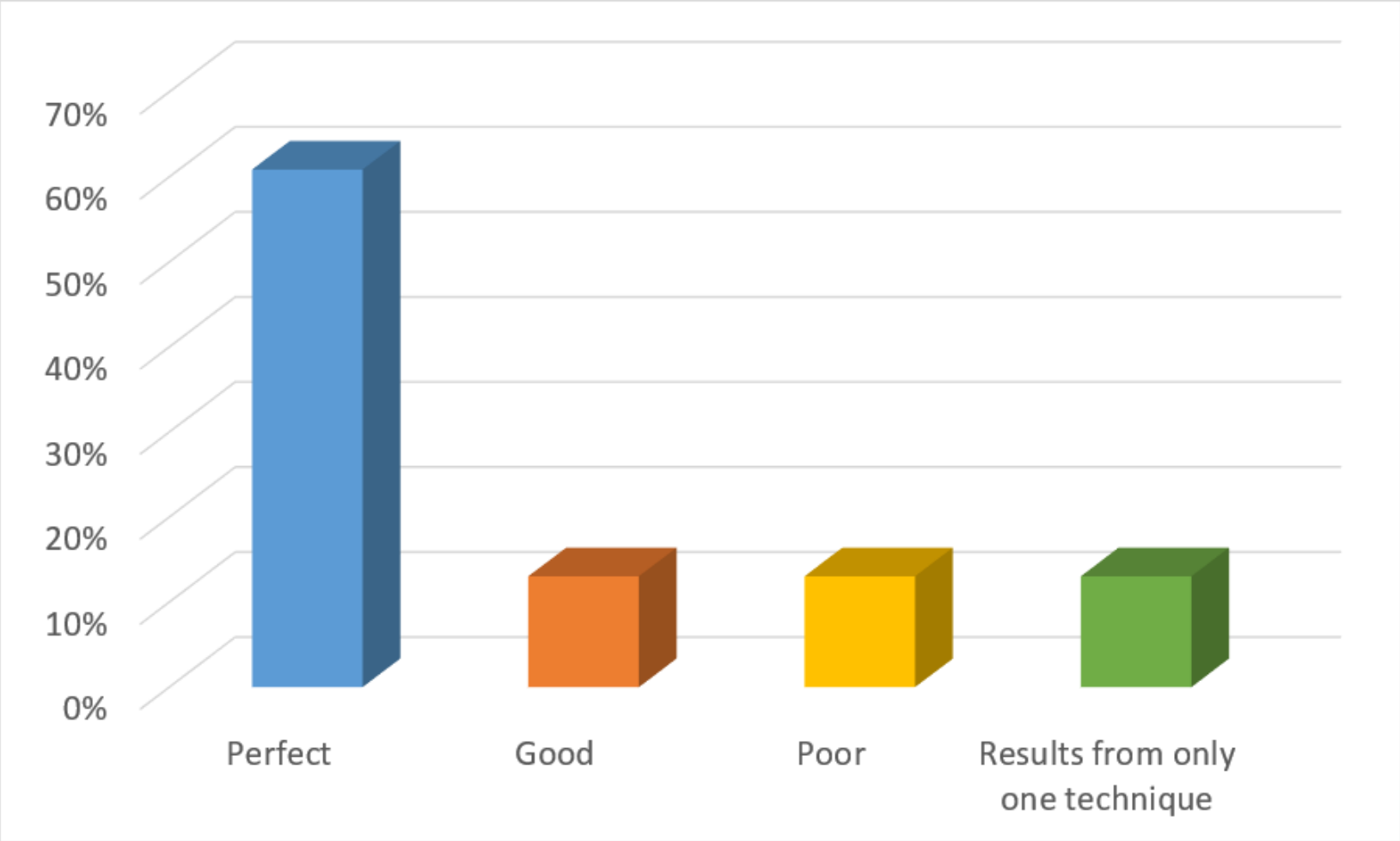
Chromatographic technique

Sensitive to molecular structure based on breakdown into fragments

Sample is completely pyrolyzed (destroyed)

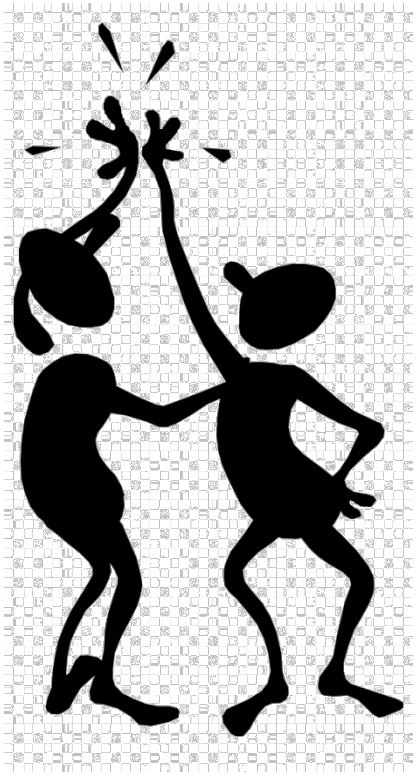
Long measurement time

How well did the three techniques match for different polymers of marine debris?



N=23

Perfect Matches



Polymer	Raman	ATR-FTIR	GC-MS
Ka'ehu T1 #2	PC	PC	PC
Ka'ehu T1 #4	PS	PS	PS
Ka'ehu T1 #31	nylon 6/6	nylon	nylon 6/6
Kahuku T2 #518	PE/PP	PE/PP	PP
Kihei T1 #15	cellulose		cellulose
Maui sea surface #43	PE	unknown PE	unknown PE
Midway #30	ABS	ABS	ABS
Waianae T1 #1	PMMA	PMMA	PMMA
Waianae T2 #22	PVC	PVC	PVC w/lycoxanthin
Waikiki T1 #1	PET	PET	PET
Waikiki T1 #12	PVC	N/A	PVC
Waikiki T2 #14	HDPE	HDPE	PE
Waikiki T3 #7	PP/$CaCo_3$		PP
Waimanalo T3 #35	CA	CA	CA

Ka’ehu T1 #2

Experimental parameters:

785 nm, 10 s int. time

S/N ratio: 48:1 (900 cm^{-1})

Database Search Result:

polycarbonate

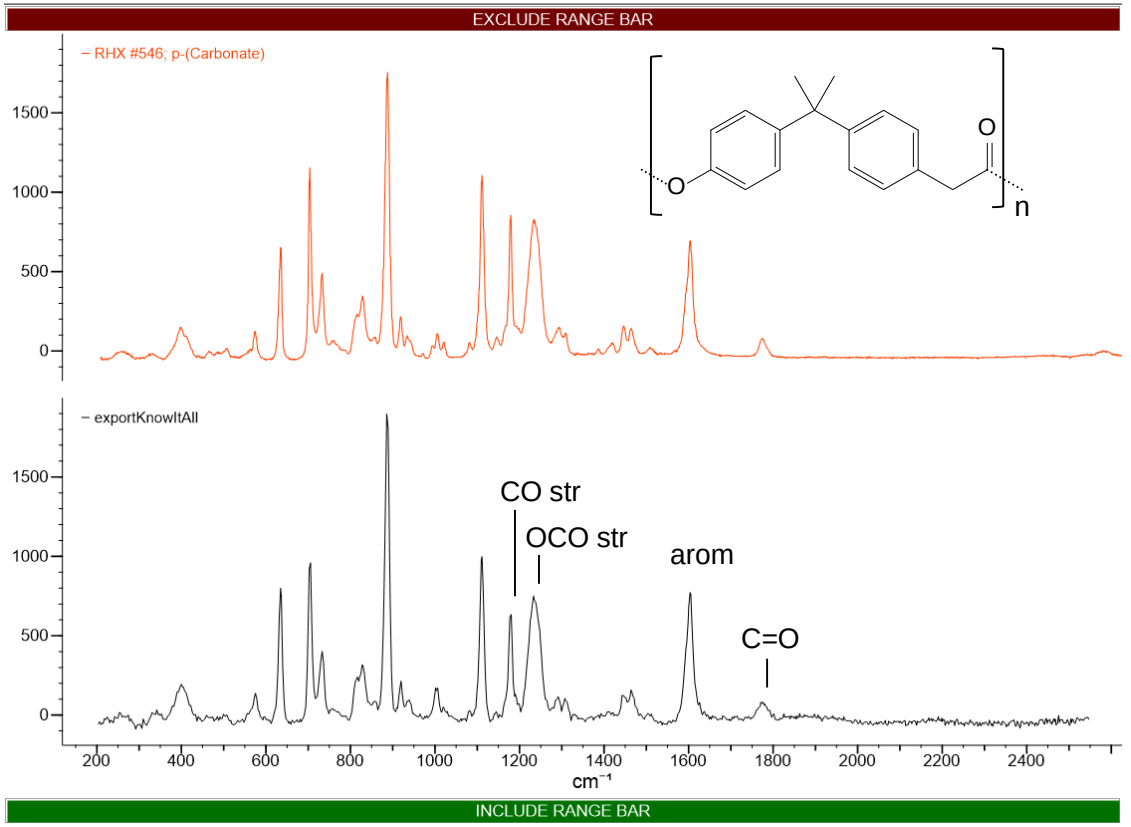
97.65% hit quality index

GC Pyrolysis Result:

polycarbonate

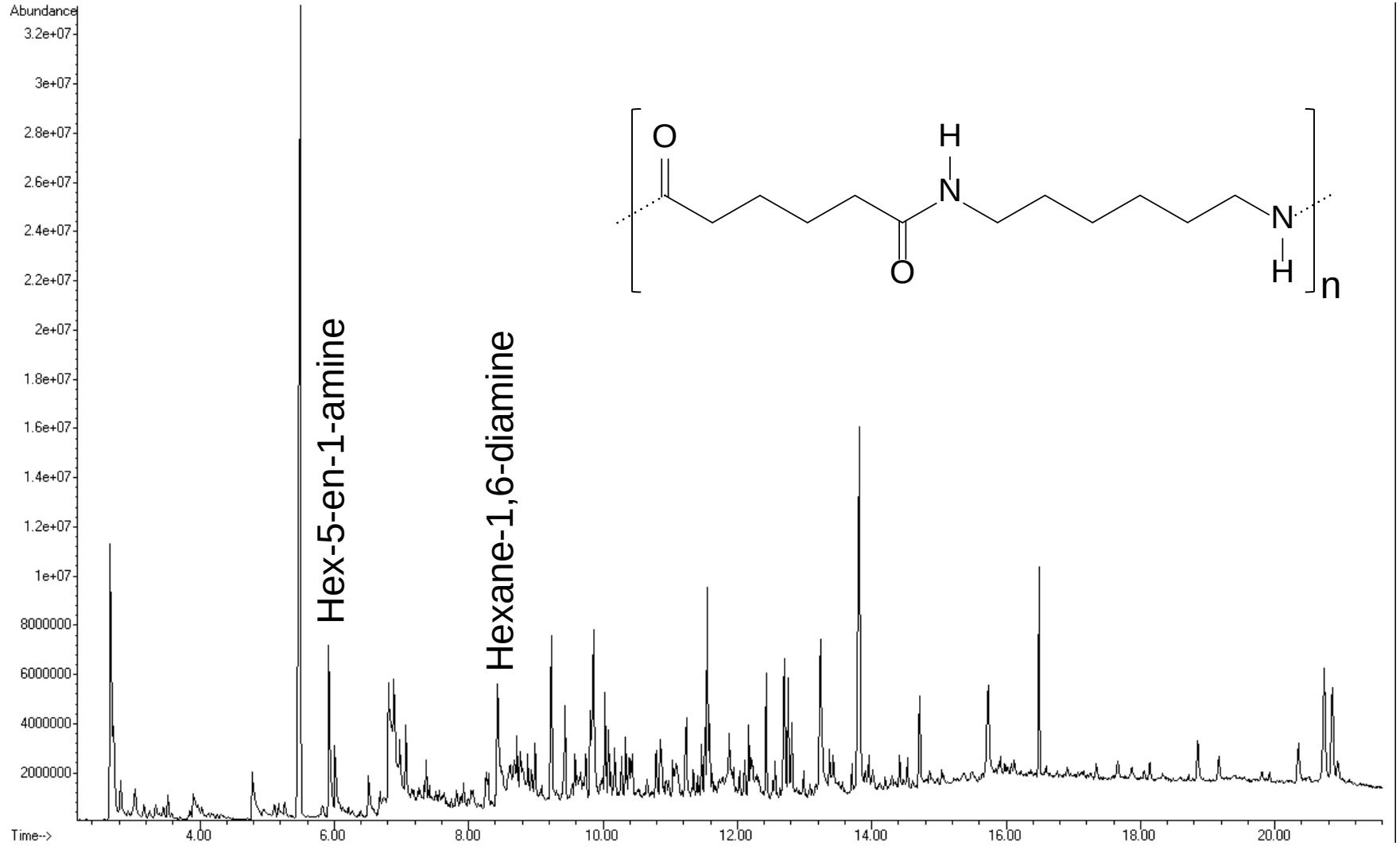
ATR-FTIR Result:

polycarbonate



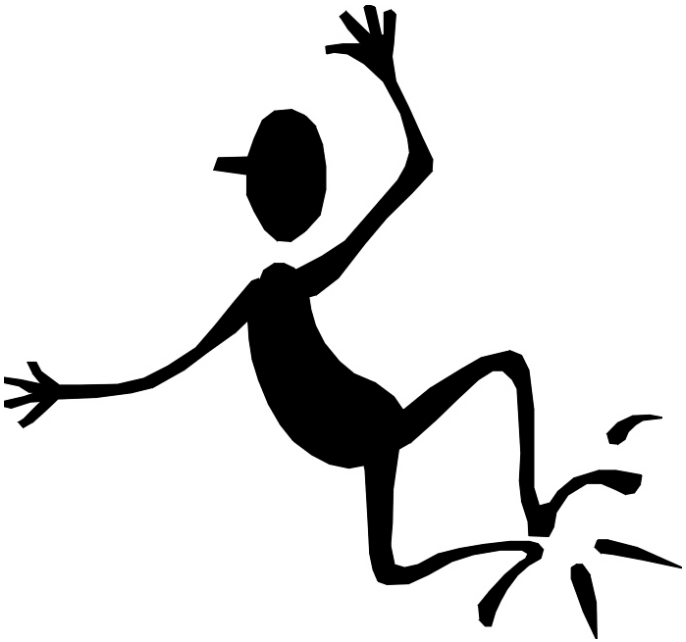
Ka’ehu #1 31

Cyclopentanone

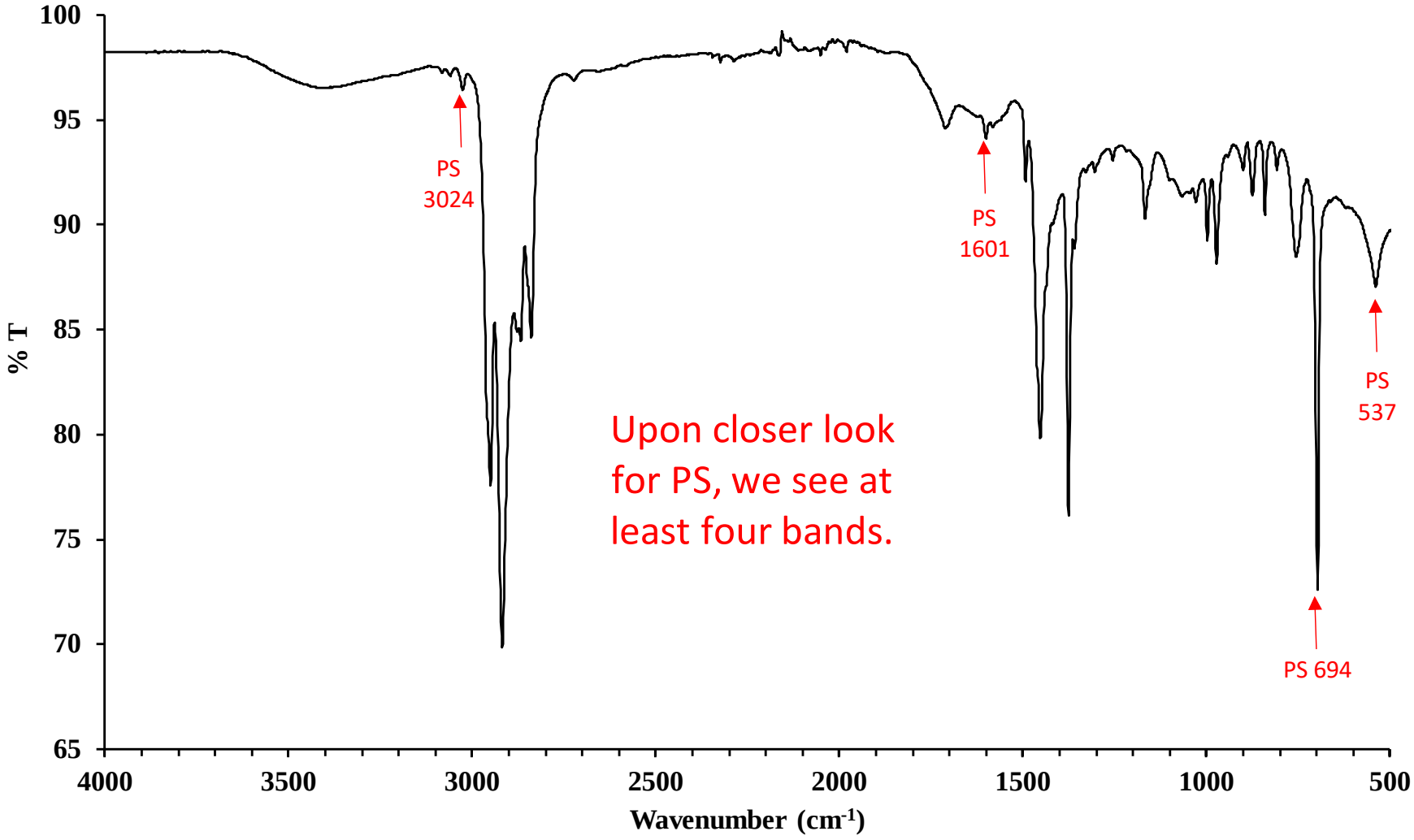


Good Matches

Polymer	Raman	ATR-FTIR	GC-MS
Lanai T2 #2	HDPE	LDPE	PE
Lanai T3 #12	copolymer	PP/PS mix	PP/PS copolymer
Waikiki T3 #2	cis-polyisoprene	Latex	Latex w/phthalate



Lanai T3 #12



Waikiki T3 #2

Experimental parameters:

785 nm, 1 s int. time

S/N ratio: 13:1 (1680 cm^{-1})

Database Search Result:

cis poly(isoprene)

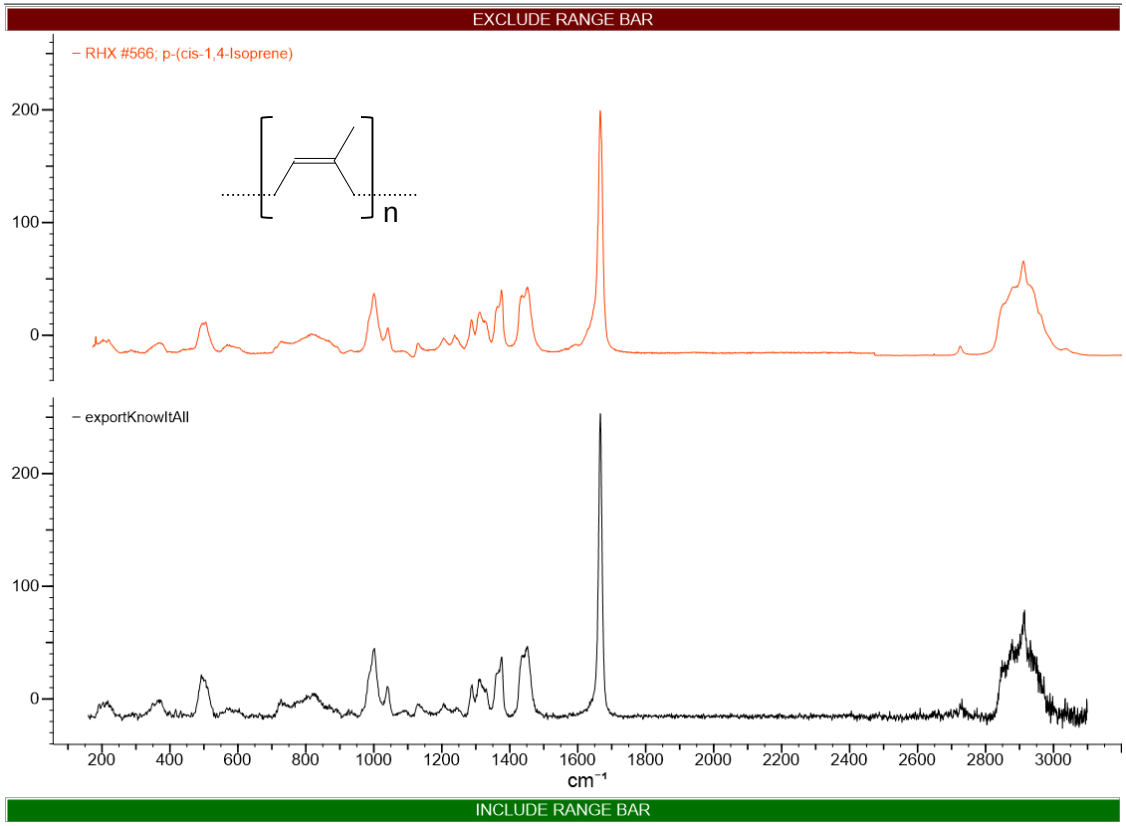
97.43% hit quality index

GC Pyrolysis Result:

Latex with phthalate additive

ATR-FTIR Result:

latex



Poor Matches

Polymer	Raman	ATR-FTIR	GC-MS
Ka'ehu T2 #5	PE	EVA	PE
Waianae T3 #26	PU		PABM
Waikiki T1 #14	PET	phthalate	PVC w/phthalate derivative

Waikiki T1 #14

Experimental parameters:

785 nm, 10 s int. time

S/N ratio: 54:1 (1600 cm^{-1})

Database Search Result:

poly(ethylene terephthalate)

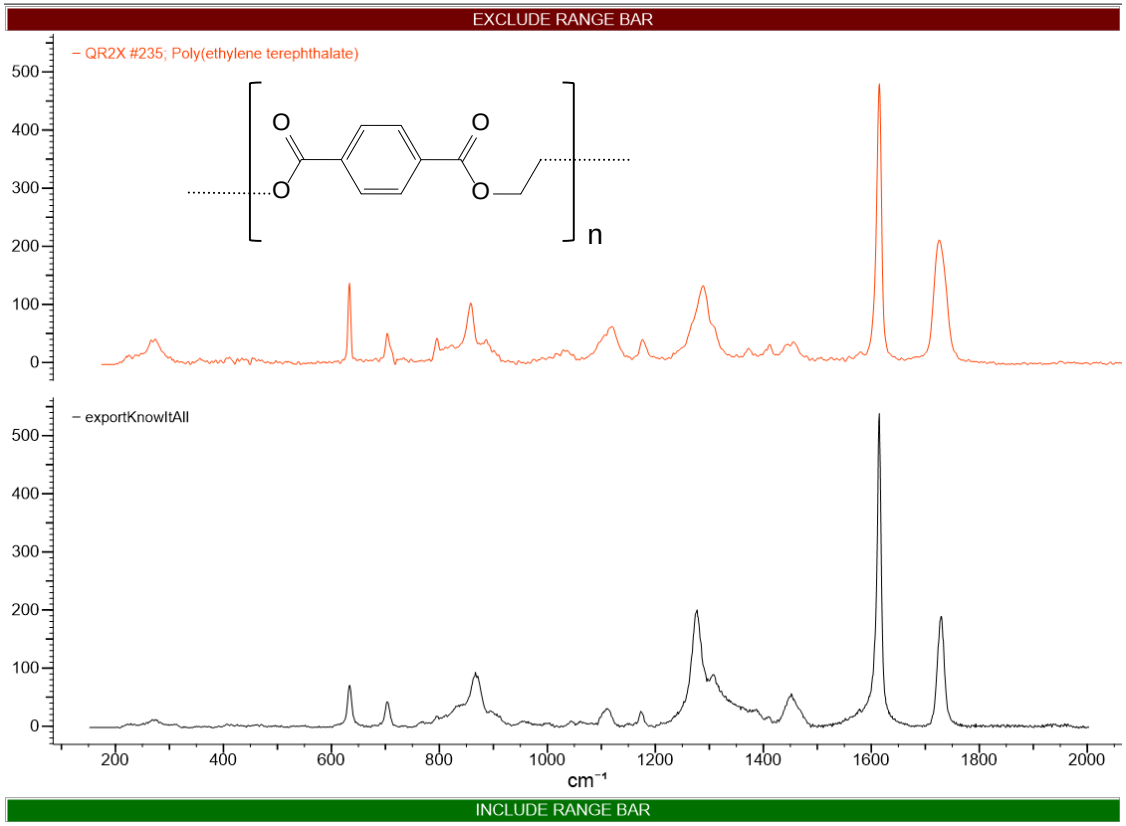
86.1% hit quality index

GC Pyrolysis Result:

PVC with phthalate derivative

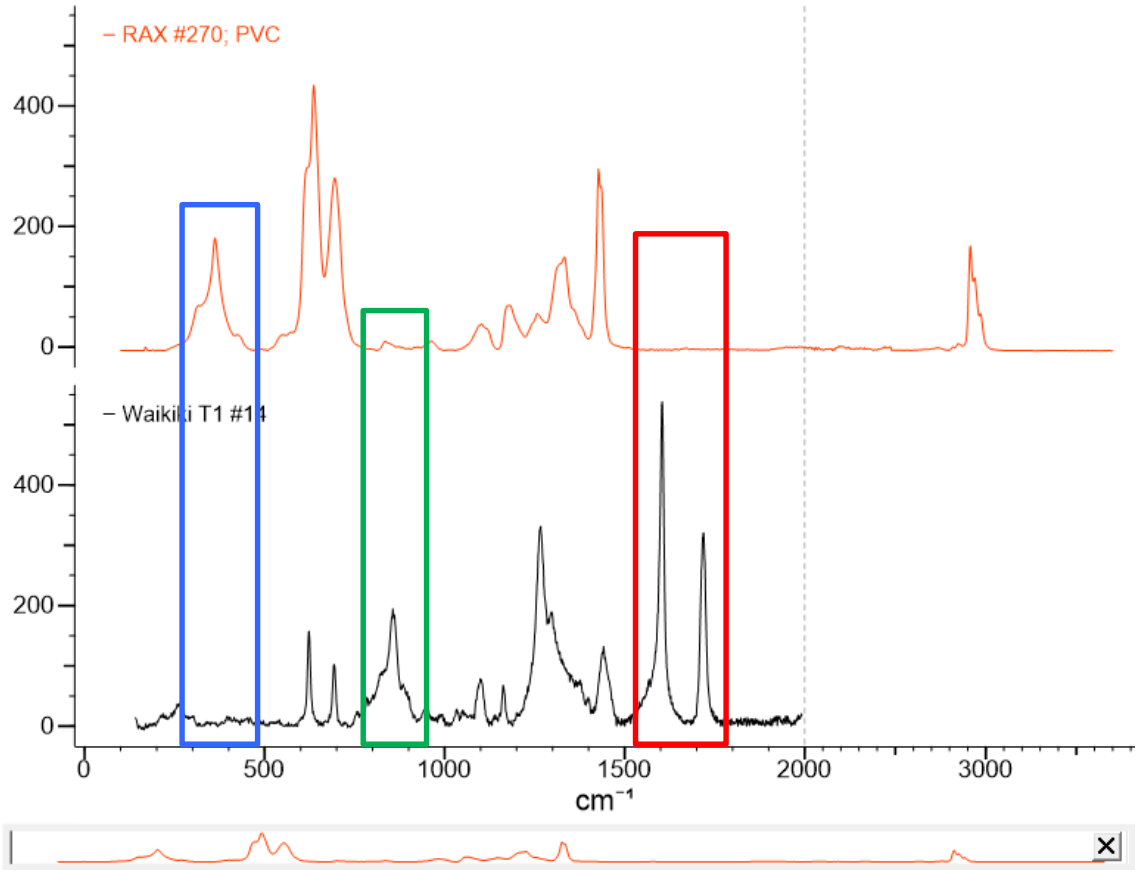
ATR-FTIR Result:

Generally phthalate



Waikiki T1 #14 – Results comparison

- Results from GC pyrolysis suggest PVC while results from Raman suggest poly(ethylene terephthalate)
- Comparison of reference spectrum of PVC with recorded Raman spectrum show clear spectral differences
  - Unknown sample has bands at 1725 and 1610 cm^{-1} that are not present in the reference
  - Bands below 500 cm^{-1} in reference spectrum are not observed in unknown
  - Band at ~850 cm^{-1} in unknown spectrum is not in reference spectrum



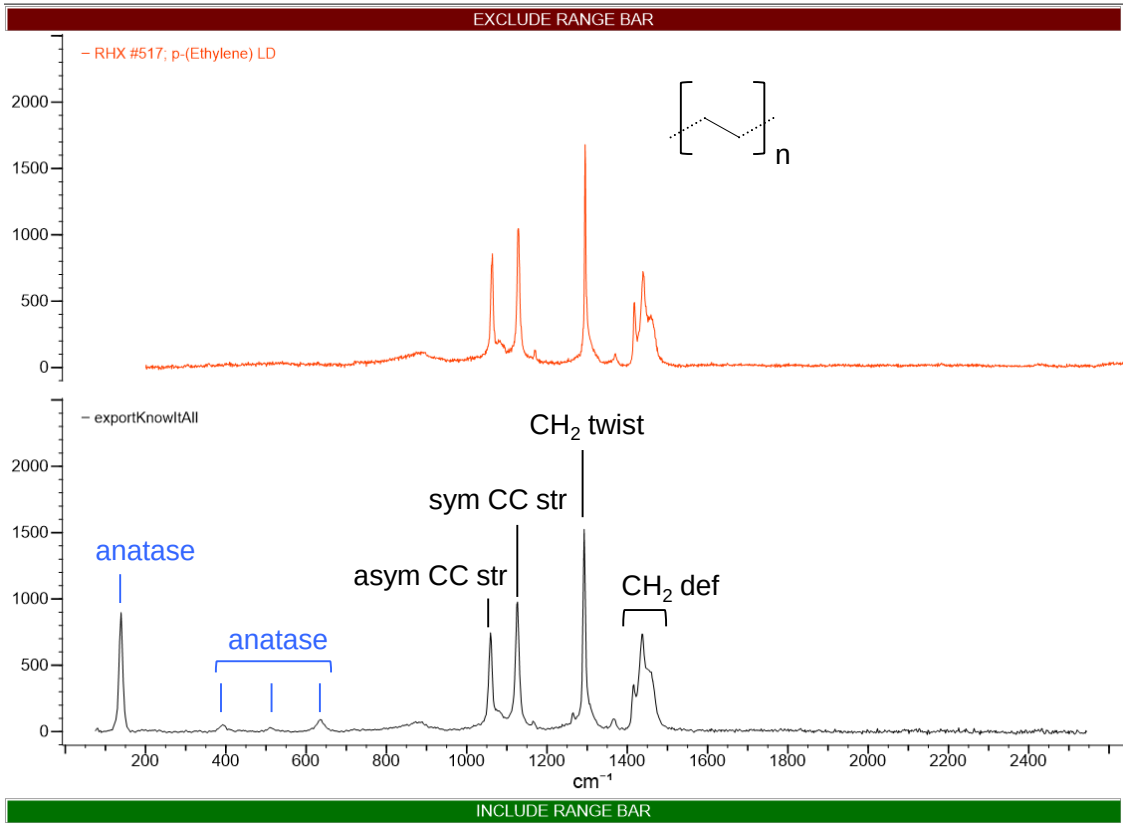
Ka’ehu T2 #5

Experimental parameters:
785 nm, 10 s int. time
S/N ratio: 3860:1 (CH str)

Database Search Result:
poly(ethylene)
95.93% hit quality index

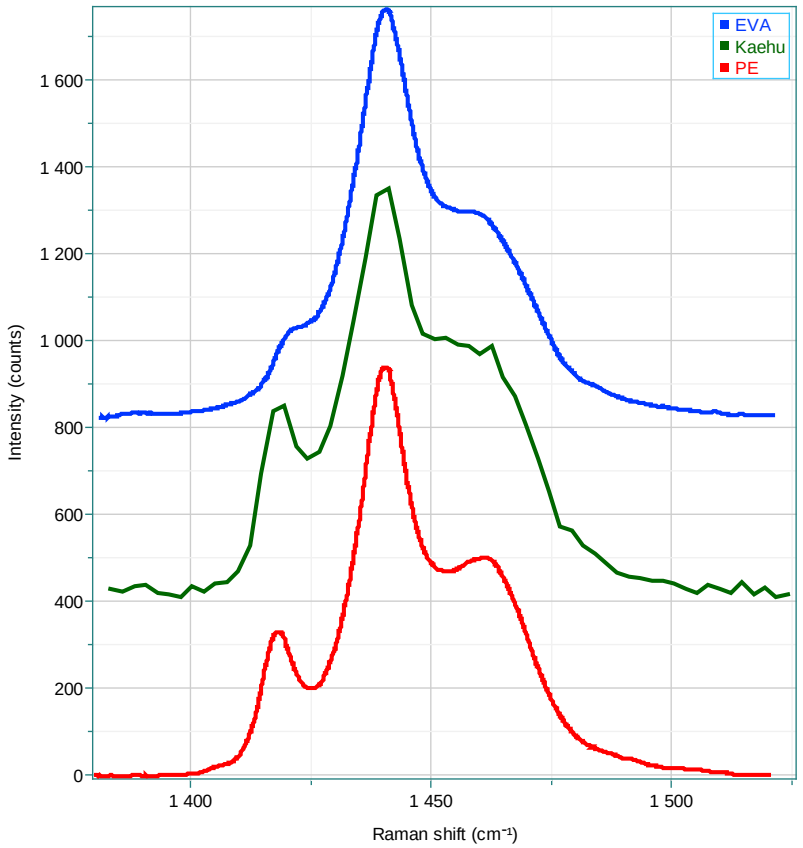
GC Pyrolysis Result:
poly(ethylene)

ATR-FTIR Result:
poly(ethylene vinyl alcohol)

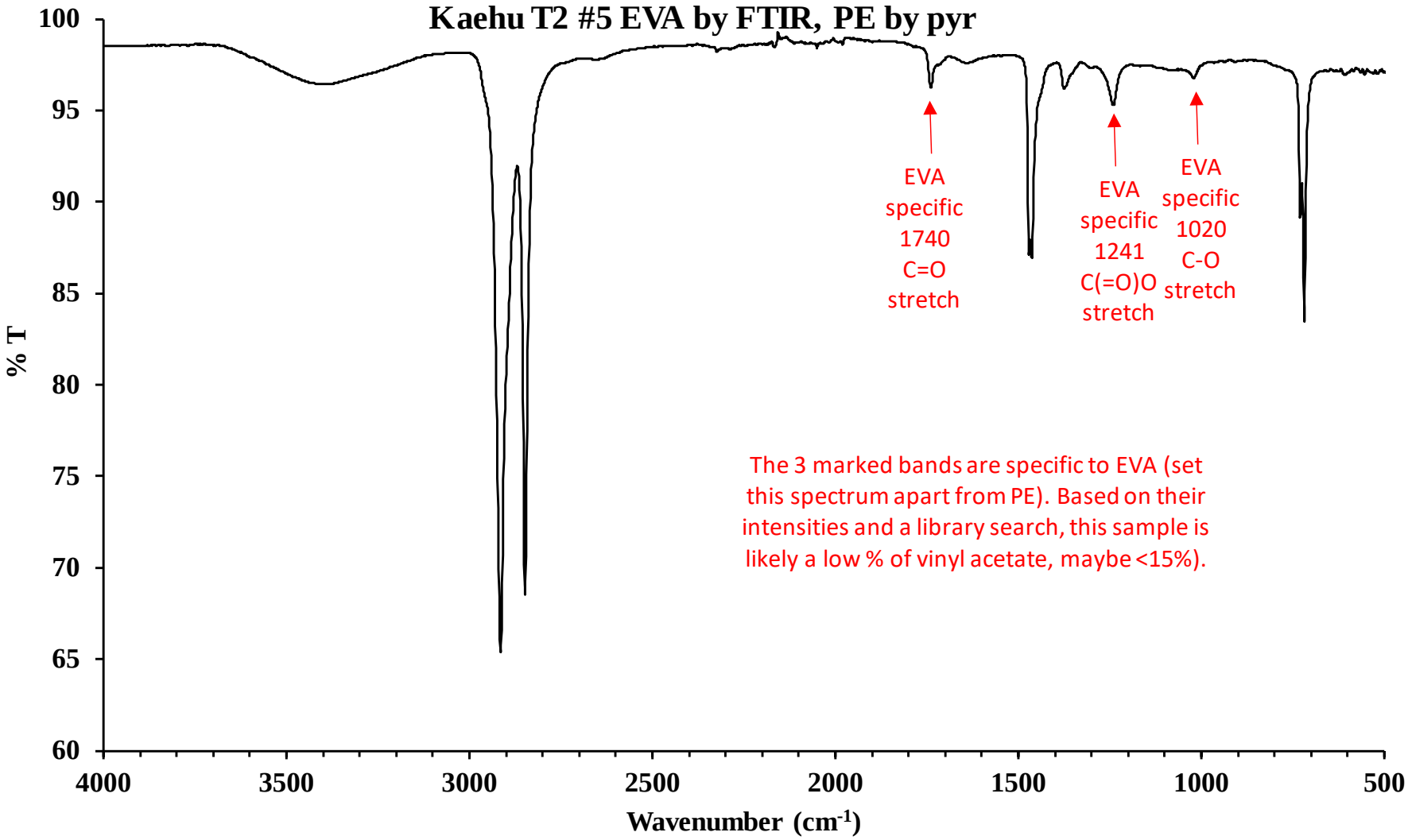


Ka'ehu T2 #5 – Results comparison

- Results from ATR-FTIR suggests EVA while results from Raman suggest poly(ethylene)
- Comparison of reference spectrum of EVA and PE with recorded Raman spectrum show some subtle spectral differences
- Band at 1450 cm^{-1} resembles bands from both EVA and PE – confident assignment using Raman spectroscopy alone is not possible

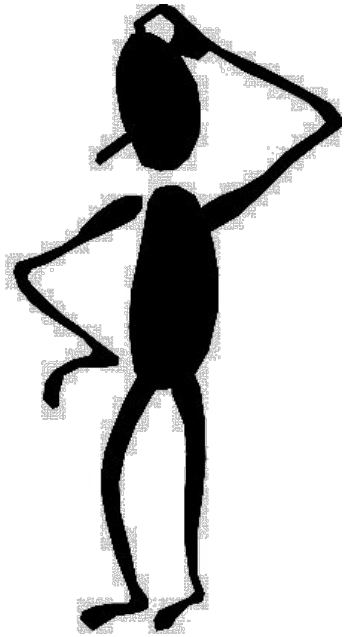


Ka'ehu T2 #5 ATR-FTIR Results



Single Technique Matches

Polymer	Raman	ATR-FTIR	GC-MS
Kihei T1 #27	n-cyclohexyl-2-benzothiazole sulfonamide		
Waianae T2 #30			SBS
Waikiki T1 #77			PS possible polymethylstyrene copolymer w/phthalate der.



Kihei T1 #27

Experimental parameters:

638 nm, 20 s int. time

S/N ratio: 100:1 (1470 cm^{-1})

Database Search Result:

n-cyclohexyl-2-benzothiazole sulfenamide

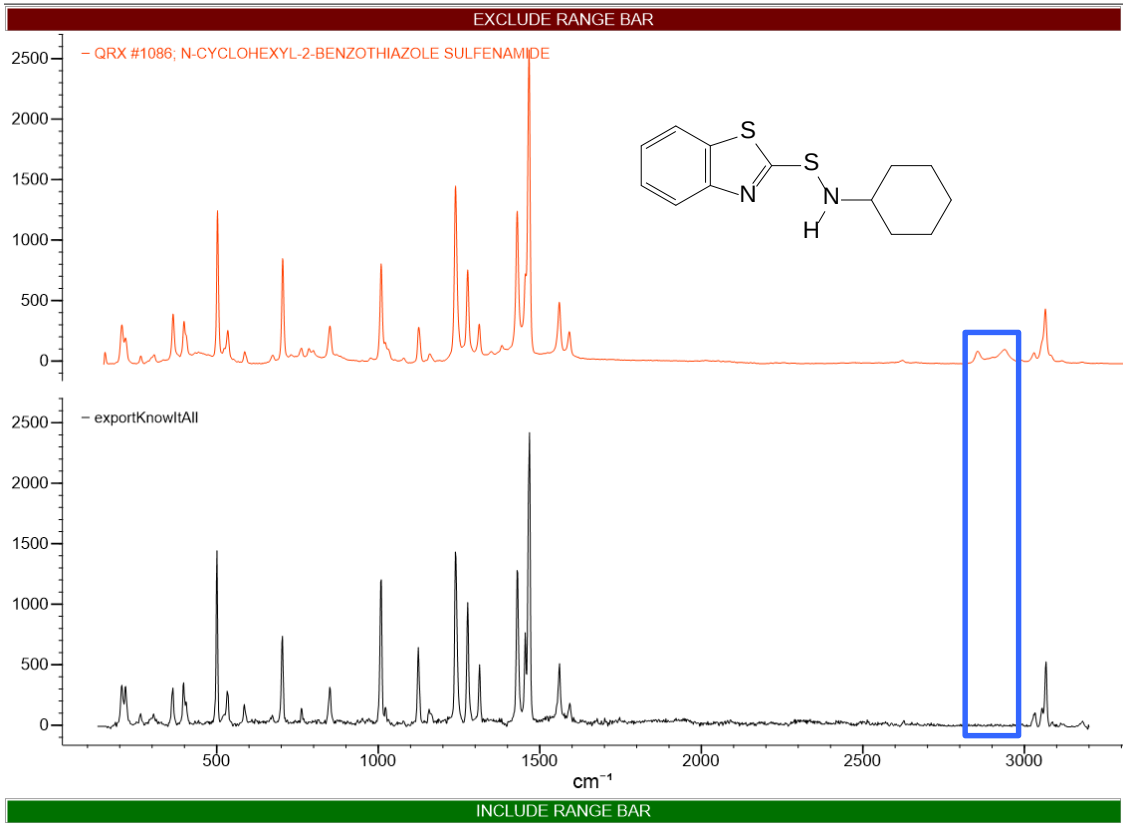
91.37% hit quality index

GC Pyrolysis Result:

N/A

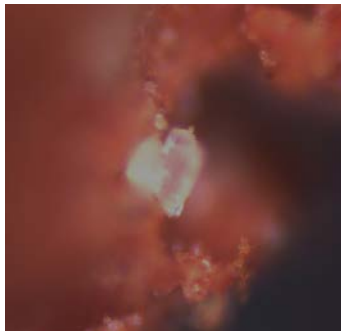
ATR-FTIR Result:

N/A



Kihei T1 #27 – Additives

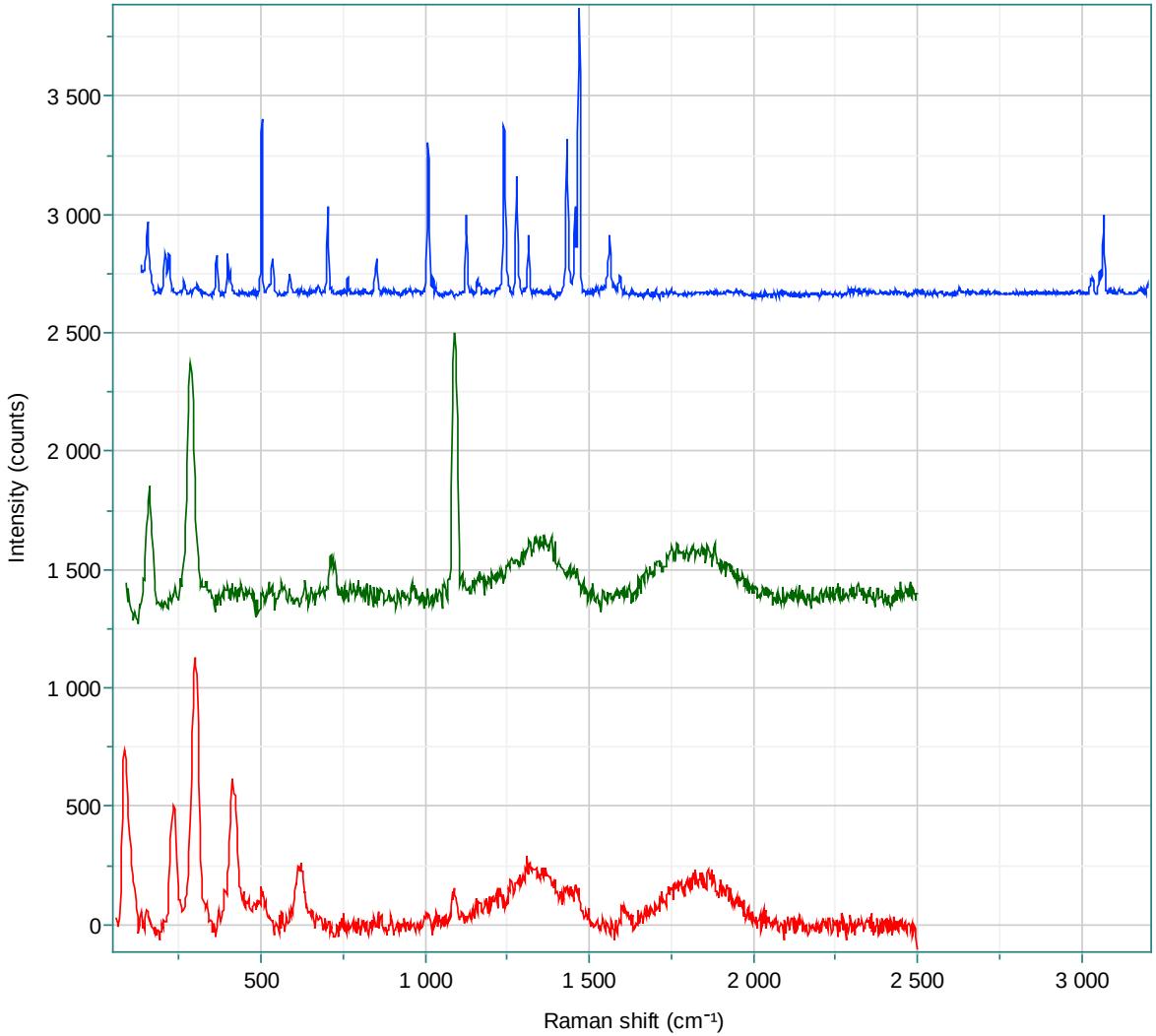
Microscopy provides spatial selectivity to probe individual components in heterogeneous samples



Sample shows evidence of two additives in addition to polymer

Iron oxide used for red coloring

Calcium carbonate for heat resistance, stiffness, and hardness



Conclusions

- 70% of measurements recorded with Raman, ATR-FTIR, and pyr. GC-MS agreed (good or perfect)
- All three methods gave good results with coarse accuracy
- Each method has its own strengths/weaknesses
- Ideally, a lab would be equipped with multiple techniques for plastic characterization

Acknowledgements

HORIBA
Explore the future

NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

NIST
National Institute of Standards and Technology

UNIVERSITY OF HAWAI'I
MĀLAMALAMA
UA MAU KE EA O KA 'ĀINA I KA PONO
1907

FLORIDA AGRICULTURAL MECHANICAL UNIVERSITY
HEAD HEART HAND FIELD
1887

SAVANNAH STATE UNIVERSITY
CONSTITUTION
1890
SAVANNAH, GEORGIA

HAWAI'I PACIFIC UNIVERSITY
HOLOMUA ME KA 'OIA'I'O

BIO-RAD

Thank you

HORIBA Scientific

Thank you

Omoshiro-okashiku

Joy and Fun

감사합니다

ありがとうございました

Dziękuję

धन्यवाद

Merci

谢谢

ขอบคุณครับ

Σας ευχαριστούμε

شُكْرا

Tack ska ni ha

Большое спасибо

Danke

Gracias