Portable Spectroscopy for Screening of Ortho-Phthalate Plasticizers in Production Line Tubing

Joshua Moskowitz[1], Katherine Carlos[2], Eric Crump[2], Timothy Begley[2], Betsy Jean Yakes[2]

[1]*University of Maryland, Joint Institute for Food Safety and Applied Nutrition, 2134 Patapsco Building, College Park, MD 20742*

[2]*U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, 5001 Campus Drive, College Park, MD 20740*

Introduction

In this work we evaluate two commercially available portable Raman spectrometers for their ability to accurately classify the ortho-phthalate group of plasticizer compounds in polyvinyl chloride (PVC) food contact production line tubing. Further, we aim to discriminate individual plasticizer compounds in the PVC tubing from a panel of multiple components. This may be accomplished through both library matching and chemometric modelling of certain "fingerprint" regions in the Raman spectra. These library and chemometric methods function via the comparison of Raman spectra between unknown food contact tubing samples and a panel of previously scanned, known tubing samples and sheet standards. This work may provide information regarding the prevalence of various plasticizers currently used in food contact dairy production line tubing.

Plasticizers Background

- Current FDA regulations authorize plasticizers for use in food contact materials in 21 CFR Parts 170-199.
- Ortho-phthalate plasticizers: butyl benzyl phthalate (BBP), diisononyl phthalate (DINP), dicyclohexyl phthalate (DCHP), dihexyl phthalate (DHP), diphenyl phthalate (DPP), di-(2-ethylhexyl) phthalate (DEHP), and diisooctyl phthalate (DIOP).
- Non-ortho-phthalate plasticizers: Di-ethylhexyl terephthalate (DEHT), acetyl tributyl citrate (ATBC), diisobutyl adipate (DIBA), and epoxidized soybean oil (ESBO).

Plasticizer	Abbreviation
Diethylhexy phthalate	DEHP
Di-isodecyl phthalate	DIDP
acetyl tributyl citrate	ATBC
Diethylhexy terephthalate	DEHT

Table 1: Table of PVC tubing plasticizers with abbreviations.

Materials and Methods

- Rigaku ResQ Progeny: 1064nm instrument
- Thermo TruScan RM: 785nm instrument
- Various plasticized PVC sheet standards
- 15 de-identified food contact production line tubing samples

Figure 1: 1064nm (Left) and 785nm (Right) portable Raman instruments, with food contact production line tubing (Middle).

- Food contact production line tubing analysis via portable Raman spectral library matching on both devices.
- Food contact production line tubing analysis via on-instrument Principal Component Analysis (PCA) chemometric modelling on the 785nm instrument.
- Unknown tubing plasticizer identification via GCMS, and subsequent addition of these samples to the on-instrument Raman spectral library for matching future unknown tubing samples.

Results

Effect of Sample Positioning on Tubing Analysis via Portable Raman

1064nm Raman instrument with adjustable nosecone

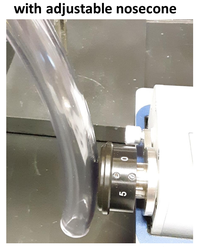


Figure 2: Tubing samples are touched against the nosecone. The optimal nosecone setting was the same for all tube samples tested thus increasing ease-of-use.

785nm Raman instrument with fixed probe cone

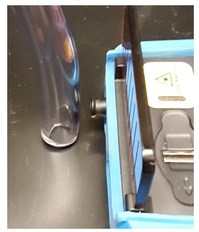


Figure 3: No adjustable nosecone available. The distance of the tube from the probe cone was found to affect plasticizer classification (see figure 4). This is because spectral peaks can be diminished depending on the exact distance the tube is from the probe cone. This holds potential to introduce user error in unknown tubing analysis.

Effect of Sample Positioning on the 785nm Portable Raman Instrument

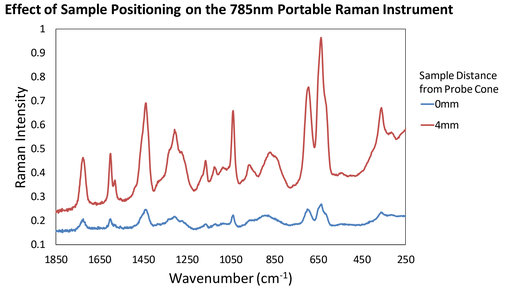


Figure 4: Raman spectra of an ortho-phthalate plasticizer in PVC at two distances from the 785nm instrument probe cone. Correct classification of this ortho-phthalate was only possible when the sample was placed ~4mm from the instrument probe cone.

Signal to Noise Evaluation of the 785nm and 1064nm Instruments

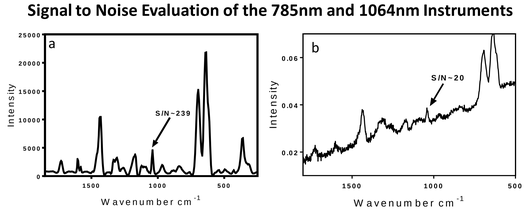


Figure 5: Raman spectra of a 20% di-isononylphthalate (DINP) in PVC sheet standard from (a) the 1064nm instrument and (b) the 785 nm instrument. The S/N was estimated for the peak at 1040 cm^{-1}. This peak results from planar ring vibrations and is indicative of an ortho-phthalate. S/N was estimated as the peak height/standard deviation of a range of wavenumbers in the flat (blank) region of the spectra.

Ortho-Phthalate Classification from Library Matching on the (a) 785nm and (b) 1064nm Instruments

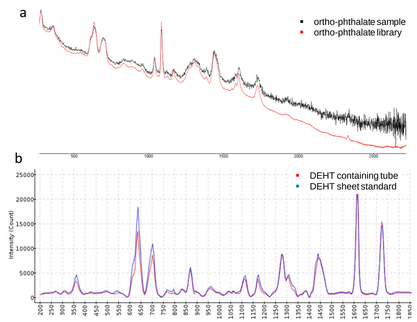
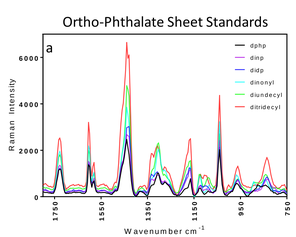


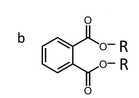
Figure 6: Library matching on the (a) 785nm and (b) 1064nm instruments. (a) A DIDP in PVC tubing sample (black) was correctly classified through comparison with a library ortho-phthalate spectrum (red). (b) A DEHT containing PVC tube (red) was matched with a DEHT sheet standard (blue), leading to non-ortho-phthalate classification.

"Moving Towards" Individual Plasticizer Discrimination

Approach:
Each of the spectra below in Figure 7 was correlated against the others. This was done over three different wavenumber ranges, to determine the optimal range for distinguishing an individual ortho-phthalate in a PVC sheet with library matching. Correlation among the spectra was measured with a R^2 value. When comparing spectra of two different phthalate compounds, a lower R^2 value is considered better because this means the different phthalates are less correlated with each other and more easily discriminated. The spectra were collected with the 1064nm instrument.

Results:
- Spectral comparison in the range of 748-1810 cm^{-1} was found to provide for the lowest R^2 values and greatest discrimination of each individual ortho-phthalate from a panel of multiple ortho-phthalate sheet standards.
- Each ortho-phthalate/PVC sheet standard was scanned on the 1064nm instrument in triplicate over the range 748-1810 cm^{-1} and correctly identified from a panel containing all the sheet standards 100% of the time.





Phthalate Abbreviation	R group
DPHP	propyl heptyl
DINP	isononyl
DIDP	isodecyl
Dinonyl	nonyl (C_9)
Diundecyl	undecyl (C_{11})
Ditridecyl	tridecyl (C_{13})

Table 2

Figure 7: (a) Raman "fingerprints" of six different ortho-phthalate plasticizers in PVC. (b) ortho-phthalate structure, with various R chain groups shown in Table 2.

Unknown Tubing Sample Analysis

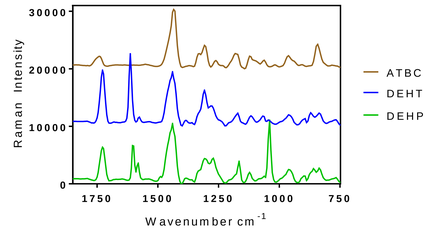


Figure 8: Raman spectra of three PVC food contact, production line tubing samples with various plasticizers. Spectra were collected on the 1064nm instrument.

Tubing Sample	GCMS Result/Raman Signature Added to Portable Instrument Library	Raman Identification (1064nm Instrument)	Year Obtained
A	DEHT	DEHT	2021
B	DEHT and ATBC	*	2021
C	DEHT	DEHT	2021
D	***	*	2021
E	***	*	2021
F	***	*	2021
G	DEHT	DEHT	2019

Tubing Sample	GCMS Result/Raman Signature Added to Portable Instrument Library	Raman Identification (1064 nm Instrument)	Year Obtained
H	DEHT	DEHT	2019
I	DEHT	DEHT	2019
J	DEHT	DEHT	2021
K	ATBC	ATBC	2021
L	ATBC	ATBC	2015
M	DEHP	DEHP	2015
N	DEHP	DEHP	2015
O	DIDP	DIDP	2015

*identification still in progress
***GCMS and DART-MS underway

Table 3: Results from unknown tubing analysis of primary plasticizers in PVC. Rapid and low-cost identification of blinded food contact tubing samples via portable Raman spectroscopy was found to be in good agreement with GCMS analysis.

Conclusions

- Sample positioning was assessed and the 1064nm instrument provided more reproducible positioning compared to the 785nm instrument.
- The 1064nm instrument was found to provide for an increased S/N.
- Library matching on both instruments yielded 100% correct classification.
- Individual plasticizers in PVC were successfully identified from a panel of multiple components over the Raman spectral region 748-1810 cm^{-1}.
- On-instrument PCA modelling (785nm instrument) provided similar plasticizer classification compared to the library matching method.
- 15 production line tubing samples were analyzed via GCMS and Raman fingerprints of these were used for on-instrument spectral library building.
- The correct plasticizer in PVC was identified from the library in 11/12 samples with the 1064nm portable Raman instrument, with the analysis of three samples still underway.
- GCMS analysis found one sample that contained two plasticizers in PVC, with Raman identification still in progress.
- Diethylhexyl terephthalate (DEHT) was found to be the most prevalent plasticizer used in the production line tubing samples obtained in 2021.
- No ortho-phthalates were found in any tubing samples obtained in 2021.