A Novel Ladder Approach for the Characterization of Diisonoyl Phthalate Using GC-MS

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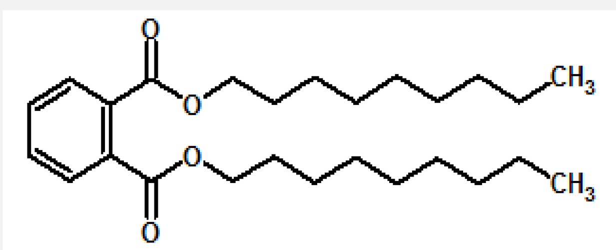
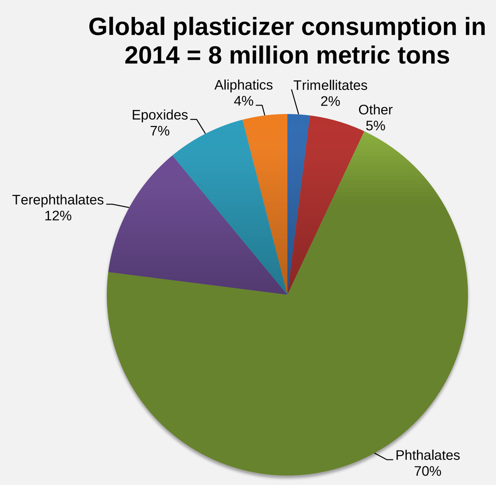
1 Introduction

Phthalates are a widely used additive in the manufacturing process of plastics, used to soften and add pliability. Despite the many benefits of using phthalates, these compounds pose potential health risks, making their quantification and characterization an important area of research. Larger phthalates such as diisonoyl phthalate (DINP) and di-n-octyl phthalate (DIOP) are generally added to plastics as a mixture of isomers. Current methods for characterization and quantification of higher order phthalates are lacking due to the complex mixture of isomers that are used in industrial plastic production. **The goal of this research is to create a novel approach for characterizing the isomeric composition of DINP by using the addition of laddering phthalate compounds with GC-MS.**

2 Phthalates





USA: Interim ban in toys that can be placed in children's mouths, child care products
EU: Prohibited in products placed in children's mouths

McCoy, M.: A Reckoning for Phthalates. Chem. Eng. News. 93, (2015).

3 Methods and Instrumentation

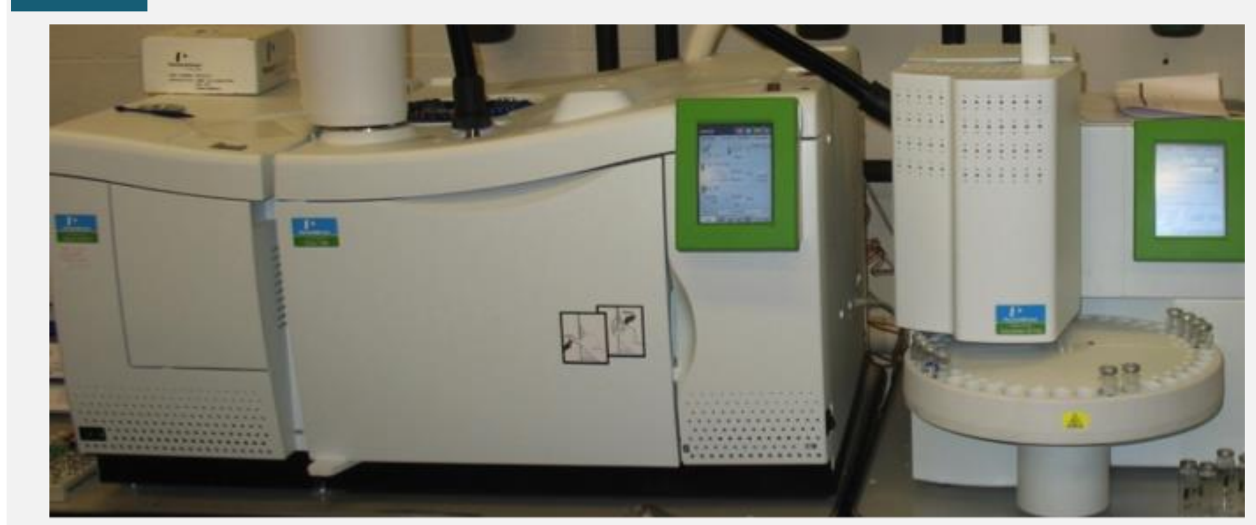


Figure 1. A picture of the GC-MS used for the experiments, equipped with a liquid autosampler.

Table 1. Conditions used for separation of phthalates mixture.
This was adapted from EPA method 8061A, Phthalate Esters by GC/ECD.

Parameter	Value
Column	PerkinElmer Elite-5MS P/N:9316282
Injector Temperature	250ºC
Temperature Ramp	150ºC hold for 0.5 min, 5ºC/min to 220ºC, 3ºC to 275ºC hold 13 min
Flow	1.43 ml/min
Split	1:5
Ionization Mode	EI+
Source Temperature	200ºC

4 Standard Phthalate Mixture

Significant separation of higher order phthalates can be easily achieved using the EPA 8061A separation method adapted for mass spectrometry. Unfortunately, commercial DINP presents as an envelope of isomeric structure, making it difficult to readily identify the specific structure/level of branching.

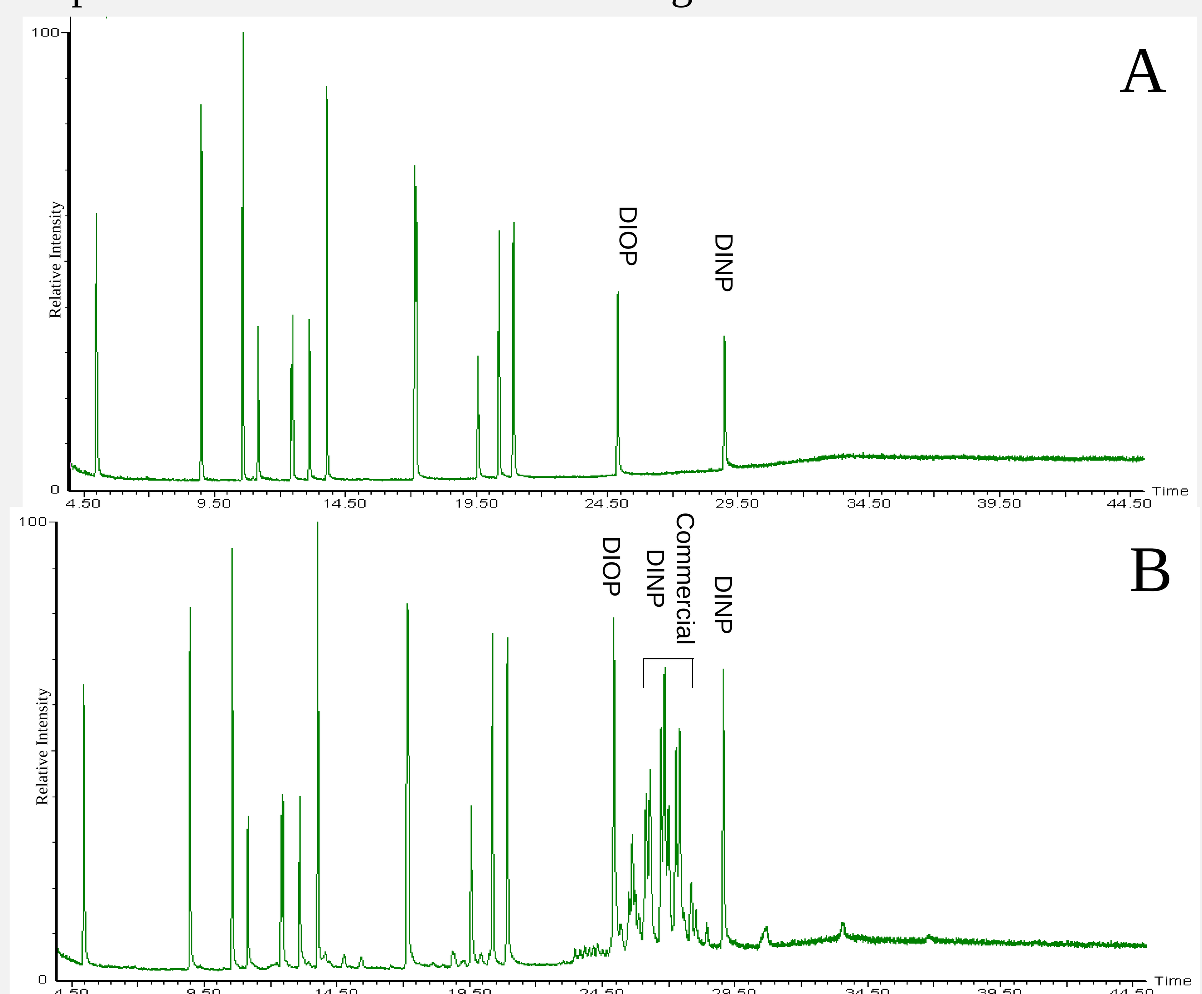


Figure 2. **A**: Standard phthalate mixture of phthalate (Restek cat # 33227), showing significant separation between the DIOP and DINP for the higher order phthalate. **B**: Mixture with spiked commercially available DINP. Note the large isomer distribution within the DIOP and DINP peaks.

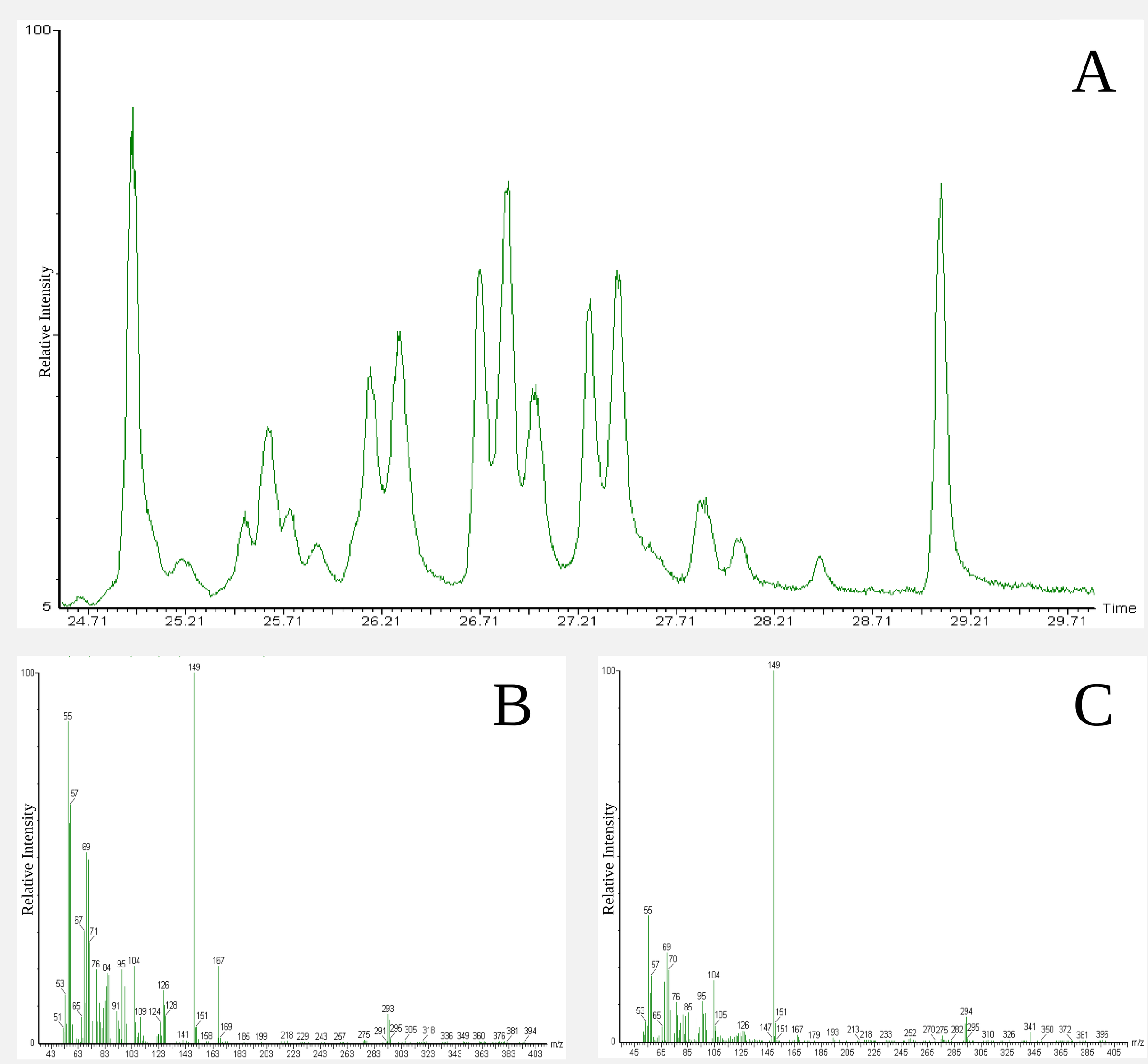


Figure 3. **A**: Standard phthalate mixture of phthalate (Restek cat # 33227) showing isomeric distribution of DINP. **B**: Mass spectrum from TIC at retention time 25 minutes, matching the NIST library for DINP. **C**: Mass spectrum from TIC at 28.5 minutes, also matching the NIST library for DINP.

5 Laddering Compounds

This approach is designed to help identify the branching involved with the higher order phthalates. Custom DINP standards were synthesized to represent an array of possible isomers which may be possible for DINP.

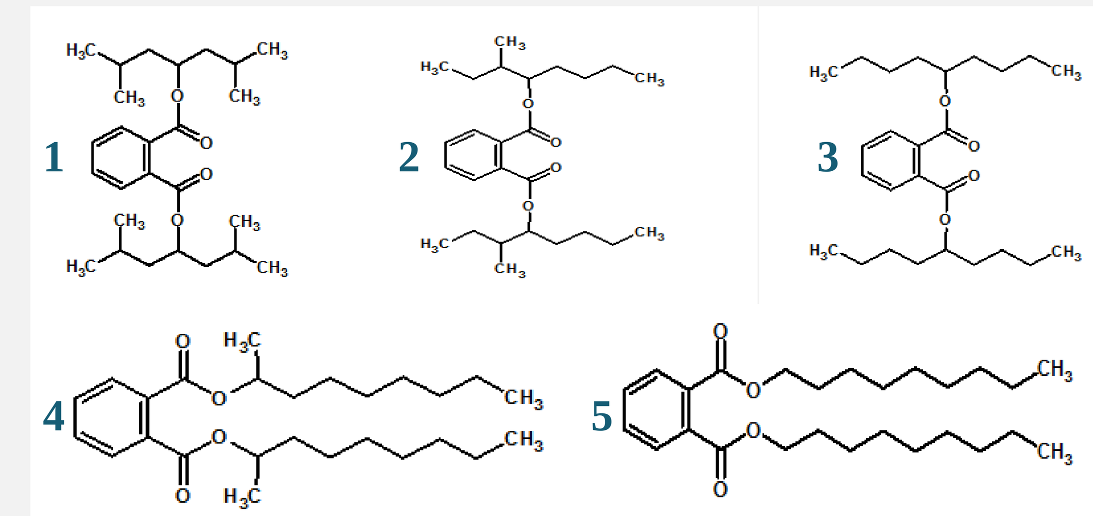


Figure 4. Structural representation of custom made DINP standards (Aurora Analytics). Various degrees of branching were requested to represent and identify the possible mixtures in the commercial phthalate.

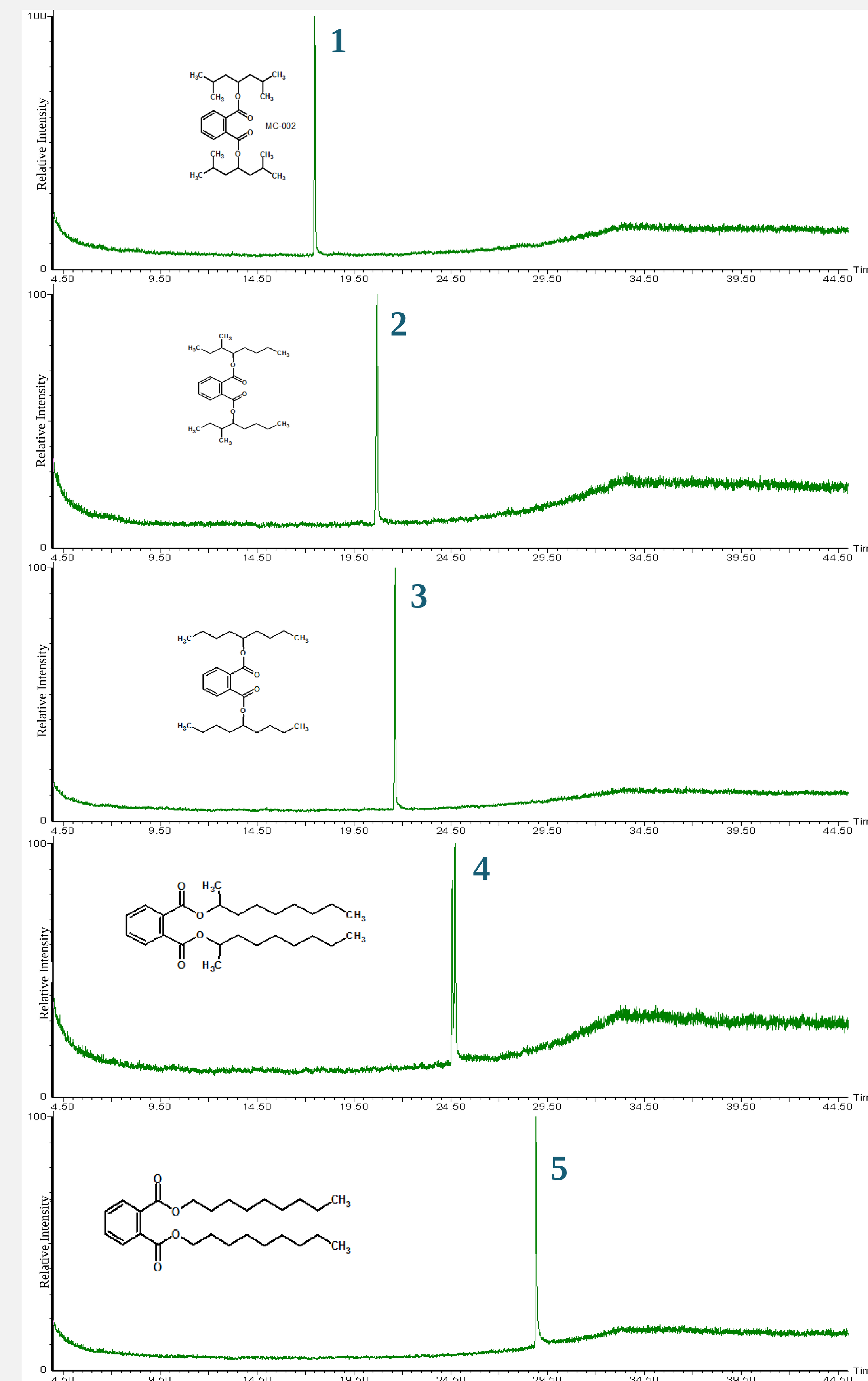


Figure 5. Phthalate standards run individually, showing that a wide range of retention times can be achieved although the compounds are isomeric.

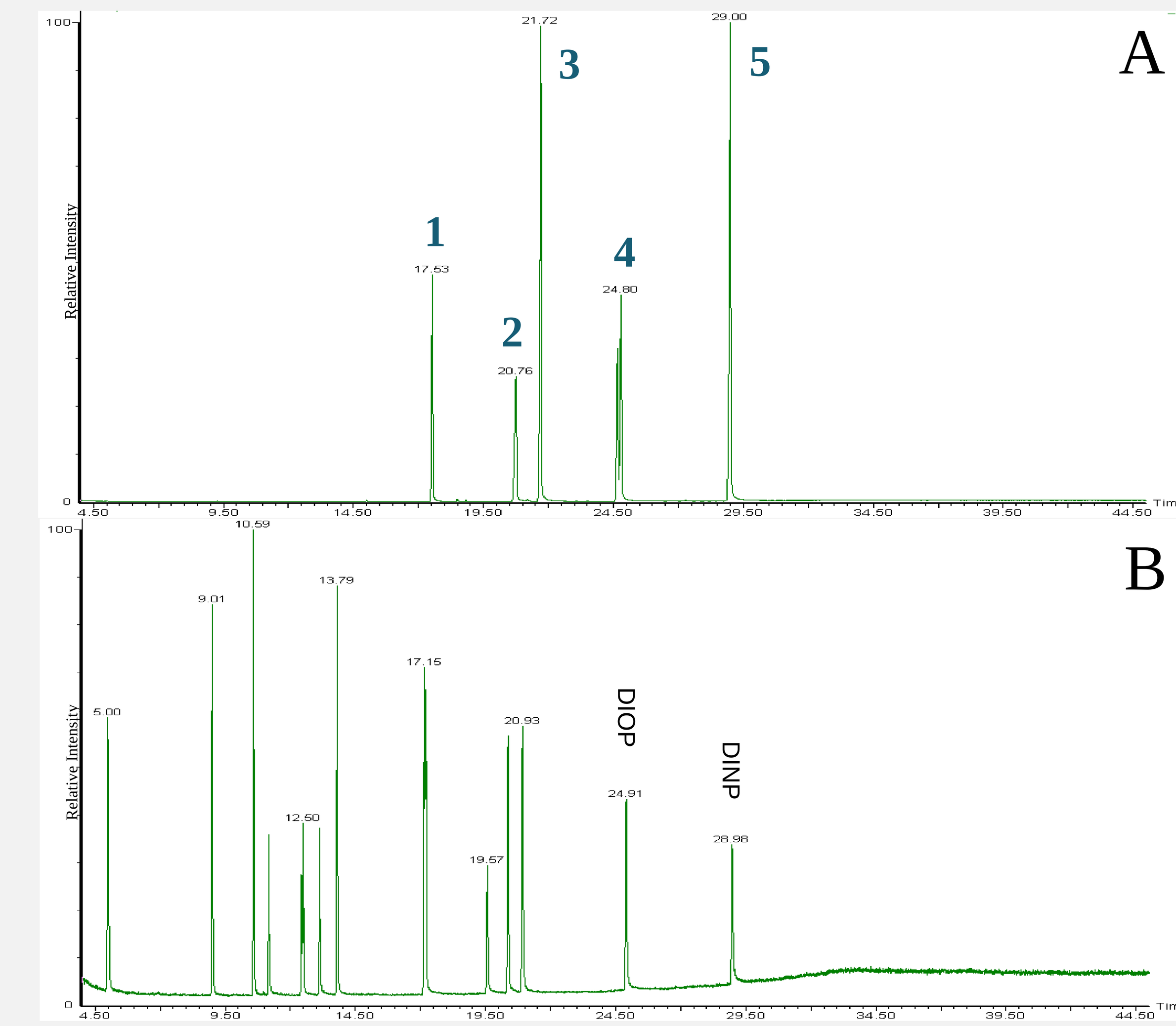


Figure 6. **A**: Chromatogram of a mixture of all five branched standards. This shows that there is a 10.5 minute difference in retention time between fully branched and linear phthalate. **B**: Chromatogram of a standard mixture showing that linear DIOP elutes after some of the highly branched DINP. This separation validates the need for ladder compounds.

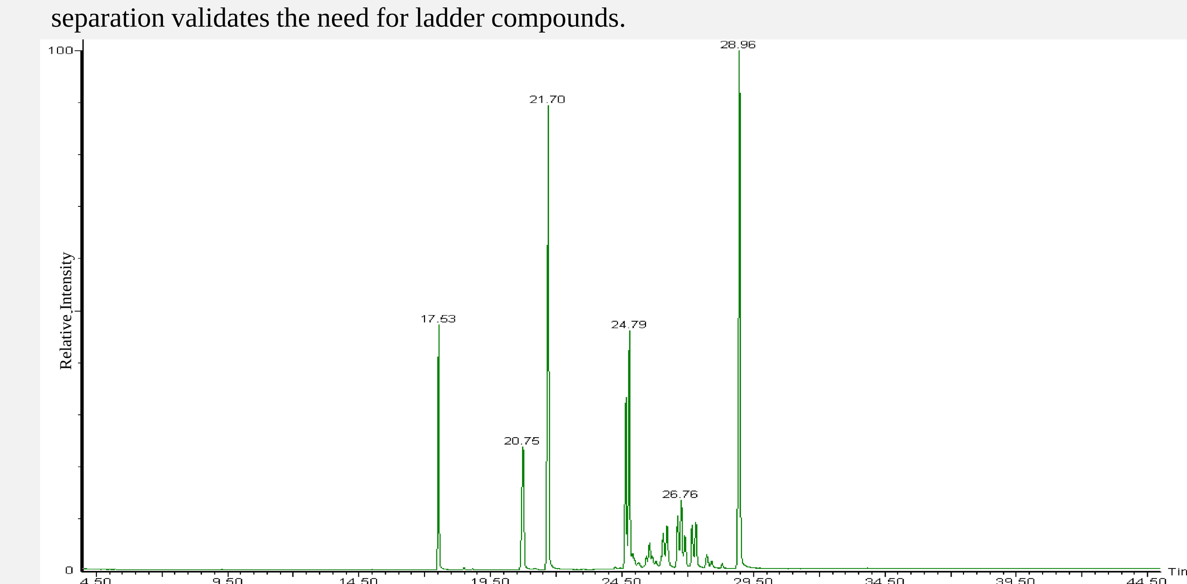


Figure 7. Chromatogram of ladder compounds run with commercial DINP. This shows that the DINP is a variation of linear to slightly branched.

6 Conclusion

This work shows that laddering compounds for higher order phthalates can be characterized by GC-MS. The information can be used to analyze the extent of isomerization within samples of phthalates, shedding light on characterizing of commercial products

Left to Right: J. Wilhide, M Georges, B. Cunning, D. McCauley, C. Gray, I. Shaffer, S. Bass, A Gray, J. Cunning, C Kwon, M. LaCourse, W. LaCourse, D. Williams, G. Winter