World Journal of Analytical Chemistry, 2026, Vol. 11, No. 1, 1-14
Available online at http://pubs.sciepub.com/wjac/11/1/1
Published by Science and Education Publishing
DOI:10.12691/wjac-11-1-1

Various Quantitative Analytical Techniques for Compositional Analysis of Short Chain Alkyl (C1-C4) Phthalate Diester Mixtures

Ronald P. D'Amelia*, Matthew Neryaev, Michael Leone, Mary T. Rooney

Chemistry Department, Hofstra University,Hempstead,NY 11549
*Corresponding author: ronald.p.damelia@hofstra.edu

Received May 08, 2026; Revised June 10, 2026; Accepted June 17, 2026

Abstract Phthalates are chemicals primarily used as plasticizers in polymers, especially polyvinyl chloride (PVC). Phthalates are also found in pharmaceuticals, personal care products, and other daily consumer goods to improve flexibility and durability. However, certain phthalates are associated with potential health risks, such as endocrine disruption and reproductive damage. The key factor in phthalate toxicity is the substance's chemical makeup; however, molecular weight (MW) influences its release and absorption upon exposure. Generally, higher MW phthalates leach less readily, whereas lower MW phthalates leach more readily. Here, we focus on the compositional analysis of pure and binary mixtures of short-chain phthalates (Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Dipropyl Phthalate (DPP), and Dibutyl Phthalate (DBP)), due to their tendency to migrate from plastic products into their surrounding environments and water sources. Gas chromatography with flame ionization detection (GC-FID), along with quantitative proton nuclear magnetic resonance (^{1}H NMR) and Fourier-transform infrared (FTIR) spectroscopy, was used to quantitatively distinguish between these compounds and determine their relative concentrations when present in binary mixtures. GC-FID chromatograms, ^{1}H NMR spectra, and FTIR spectra were first obtained using pure phthalates (DMP, DEP, DPP, and DBP), and then for 6 sets of binary mixtures of varying gravimetric weight percent. GC-FID produced fully resolved chromatograms, while ^{1}H NMR and FTIR provided chemically specific fingerprints unique to each phthalate, with deconvolution applied to overlapping peaks to aid quantification. Quantification based on integrated peaks and spectral intensities showed a strong linear correlation between gravimetrically achieved weight percents and experimentally calculated weight percents. This correlation confirms the utility of GC, ^{1}H NMR, and FTIR in the identification and quantification of these phthalates.

Keywords: *Gas Chromatography (GC), Protonnuclear magnetic resonance spectroscopy (1HNMR), Fourier-transform infrared spectroscopy (FTIR), short-chain phthalate diesters, dimethylphthalate (DMP),diethyl phthalate (DEP), dipropylphthalate (DPP), dibutyl phthalate (DBP)*

Cite This Article: Ronald P. D'Amelia, Matthew Neryaev, Michael Leone, and Mary T. Rooney, "Various Quantitative Analytical Techniques for Compositional Analysis of Short Chain Alkyl (C1-C4) Phthalate Diester Mixtures." *World Journal of Analytical Chemistry*, vol. 11, no. 1 (2026): 1-14. doi: 10.12691/wjac-11-1-1.

1. Introduction

Phthalate diesters are a type of manufactured organic chemical widely used as plasticizers to increase the flexibility and durability of polymeric materials, particularly polyvinyl chloride (PVC) products used across consumer and industrial applications. Due to their broad utility, phthalate diesters have also been used in products such as food-contact materials, medical tubing, and other consumer goods. Due to their high production volume and broad commercial use, phthalates remain among the most widely discussed plastic additives in environmental and human exposure literature. [1,2,3]

A major concern is that phthalate diesters are not chemically incorporated into the polymer backbone, allowing them to be released from materials over time through processes such as leaching and migration. This behavior motivates ongoing monitoring of phthalate diesters in contexts where leaching and migration may contribute to human exposure. This includes food contact applications and other everyday scenarios. [2,4,5,6]

Certain phthalates have been associated with different biological effects, including endocrine disruption and reproductive toxicity, which can lead to a regulatory interest in characterizing these compounds. [3,7,8,9,10] In addition, molecular weight (MW) can influence the leaching and migration behavior of phthalates. Generally, lower-MW phthalates tend to migrate and leach more readily than higher-MW phthalates, thereby making them relevant for exposure and potential contamination studies. [6,10] Figure 1 below shows a simple organic reaction for the synthesis of synthetic phthalate diesters, which may be synthesized for a variety of uses.

Analytically, many phthalate diesters pose a challenge because they share a very similar structure and differ primarily in carbon chain length, leading to similar spectroscopic features when present as mixtures. Multiple analytical techniques are required to differentiate these diesters in a binary mixture. Established analytic techniques include gas and liquid chromatography (including GC-FID), Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR), and Proton Nuclear Magnetic Resonance (^{1}H NMR).[11,12,13] Some or all of these techniques have previously been applied to the analysis of structurally comparable organic compounds, including short-chain phenyl esters, oleate esters, benzyl esters, and cinnamyl esters, supporting the broader utility of these methods for ester mixture analysis.[14,15,16,17,18,19,20]

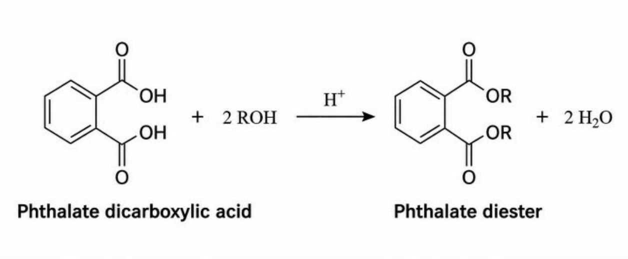

Figure 1. Acid-catalyzed Fischer esterification of phthalic acid with 2 equivalents of an alcohol (ROH) to form a generic phthalate diester and 2 equivalents of water; R represents an alkyl group

Although environmental and consumer exposure to phthalates often involves trace-level concentrations in complex matrices, the present study was designed as a foundational compositional calibration analysis model of prepared binary phthalate mixtures.

Although phthalate diesters have been widely studied using chromatographic methods, previous literature has not on the controlled compositional analysis of structurally similar short-chain phthalate diester mixtures using multiple complementary analytical techniques. Previous work has applied spectroscopic methods to the compositional analysis of related ester mixtures, including short-chain fatty acid esters, oleate esters, phenyl esters, and cinnamyl esters. The present study extends this approach to short-chain phthalate diesters by evaluating GC-FID, FTIR-ATR, and ^{1}H NMR spectroscopy for the identification and quantification of DMP, DEP, DPP, and DBP in gravimetrically prepared binary mixtures.

In this study, we focus on the compositional analysis of pure compounds and binary mixtures of four short-chain phthalate diesters: dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), and dibutyl phthalate (DBP) as shown in Figure 2. To evaluate the performance of GC-FID, FTIR-ATR, and ^{1}H NMR spectroscopy for quantitative identification and determination of relative concentrations across binary mixtures, these analytical techniques were used to determine concentrations in known-composition mixture and compare the calculated values to the known gravimetric weight percents.

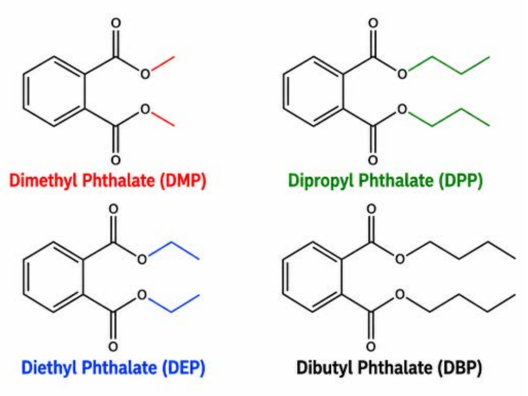

Figure 2. Structures of the four phthalate diesters used in the current study: dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), and dibutyl phthalate (DBP)

2. Materials and Methods

2.1. Experimental Materials

All the phthalate diesters were purchased as liquids from AmBeed, Thermo Scientific, and TCI. The reported percent purity was 99% for dimethyl, diethyl, and dibutyl phthalate and 98% for dipropyl phthalate. All four reagents were pipetted directly from their containers and utilized without further purification.

2.2. Sample Preparation

Twenty-four 5 mL binary mixtures of dimethyl phthalate, diethyl phthalate, dipropyl phthalate, and dibutyl phthalate were prepared in labeled 7 mL vials as outlined in Table 1. All of the dry, labeled 7 mL vials were weighed before adding any of the phthalates. Each phthalate was added with an Eppendorf series 2100 research 500 – 5000 μL pipette. After adding the specific amount of phthalate, the vial's mass was recorded with an analytical balance with 0.1 mg precision. These masses were then used to calculate the weight percent composition of each component in the binarymixtures using equation (1):

$$\%composition = \frac{M_x}{M_x + M_y} \times 100\#$$

M_x and M_y represent the mass (g) of each phthalate diester.

Table 1. Phthalate Diester Binary Mixtures

Volume Ratio	Gravimetric Weight Percent	
DMP:DEP	DMP	DEP
0 : 5mL	0	100
1 : 4mL	21.02	78.98
2 : 3mL	41.64	58.36

Volume Ratio	Gravimetric Weight Percent	
3 : 2mL	61.32	38.68
4 : 1mL	80.21	19.79
5 : 0mL	100	0
DMP:DPP	DMP	DPP
0 : 5mL	0	100
1 : 4mL	20.3	79.7
2 : 3mL	43.71	56.29
3 : 2mL	58.57	41.43
4 : 1mL	82.27	17.73
5 : 0mL	100	0
DMP:DBP	DMP	DBP
0 : 5mL	0	100
1 : 4mL	18.81	81.19
2 : 3mL	43.82	56.18
3 : 2mL	65.04	34.96
4 : 1mL	81.51	18.49
5 : 0mL	100	0
DEP:DPP	DEP	DPP
0 : 5mL	0	100
1 : 4mL	19.47	80.53
2 : 3mL	39.96	60.04
3 : 2mL	61.63	38.37
4 : 1mL	81.96	18.04
5 : 0mL	100	0
DBP:DPP	DBP	DPP
0 : 5mL	0	100
1 : 4mL	19.97	80.03
2 : 3mL	38.96	61.04
3 : 2mL	59.81	40.19
4 : 1mL	79.58	20.42
5 : 0mL	100	0
DEP:DBP	DEP	DBP
0 : 5mL	0	100
1 : 4mL	18.86	81.14
2 : 3mL	37.92	62.08
3 : 2mL	58.05	41.95
4 : 1mL	80.67	19.33
5 : 0mL	100	0

2.3. Gas Chromatography – Flame Ionization Detection (GC-FID)

Gas Chromatograms via. Flame Ionization Detection (GC–FID) were obtained using an Agilent 6890N GC–FID equipped with an HP-5 Agilent capillary column (30m x 0.32 mm x 0.25 um) containing a 5% phenyl 95% methyl siloxane stationary phase. The carrier gas was Helium with a constant flow of 4.0 mL/min. The front inlet had a split ratio of 10:1 with a flow rate of 40.0 mL/min. The front inlet temperature was 225ºC with the pressure at 20.0 psi. The total flow was 45.0 mL/min. The oven had an equilibration time of 1.00 min and was set at an initial temperature of 120ºC and the final temperature set at 215ºC with a ramp rate of 5.00ºC per minute. The final temperature was held for 1.00min. and then the oven climbed to a final temperature of 290ºC with a ramp rate of 50ºC. The GC oven temperature program was run to a final analytical temperature of 215 °C. After completion of the analytical separation, the oven temperature was increased to 290 °C as a post-run bake-out step to remove residual phthalate material from the column before the next injection.The total run time was 23.5 minutes. The flame ionization detector (FID) was set at a temperature of 250ºC, hydrogen flow at 30.0 mL/min, air flow of 400.0 mL/min, and inlet temperature of 225ºC. The FID had a constant makeup flow at 25.0 mL/min with N_2 gas. The detector signal had a data rate of 20Hz. Data was collected using Agilent OpenLabChemStation CDS software. Each chromatogram was analyzed using both Chemstation and a MATLAB_R2025 script (MathWorks Inc., Natick, MA) developed in-house. Relative concentrations of components of binary mixtures were calculated using the formula:

$$\%component\,"x" = \frac{A_x}{A_x + A_y} \times 100\#$$

where A_x and A_y are the area under the peakfor each component of the binary mixture based on the GC chromatogram.

2.4. Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Fourier-Transform Infrared Spectroscopy (FTIR) spectra were obtained using a Bruker® Alpha-P FTIR model spectrometer with platinum attenuated total internal reflectance (ATR) quick snap module containing a diamond crystal. The Alpha-P had a Michelson interferometer with a SiCglobar as the IR source, and the time dependence of the IR intensity was measured with a pyroelectric DTGS detector. Each sample was analyzed by pressing 10 μL of the sample between the anvil and the diamond crystal. Each final spectrum represents the average after 24 scans at a resolution of 4 cm^{-1} after a background measurement (ambient air) was subtracted. Bruker® OPUS software version 7.0.122. was used to collect individual spectra, and then the spectra were processed using a MATLAB R2025 script developed in-house. Relative concentrations of components of binary mixtures were calculated using the formula:

$$\%component\,"x" = \frac{H_x}{H_x + H_y} \times 100\#$$

where H_x and H_y are the heights of selected peaks unique to each component of the binary mixture based on the FTIR spectrum.

2.5. Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR):

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) spectra were obtained using a 400 MHz JEOL ECS-400 NMR spectrometer. The short-chain phthalate diesters exist as liquids at room temperature, so samples were run neat and in the absence of any deuterated solvent. Prior to running the samples, the NMR was gradient shimmed on ethyl benzene (5%) in deuterated chloroform ($CDCl_3$). Each sample was run as a single pulse 1D proton NMR experiment having a 0.25 Hz resolution and a relaxation delay of 5 seconds. 16 scans were collected per sample. The acquisition time was 2.73 s. JEOL Delta NMR control software version 6.0.0 (Windows OS) was used to collect spectra which were then processed using MATLAB scripts (MathWorks Inc., Natick, MA) developed in-house. The script takes the raw FID and performs a Fourier transform, a peak picking routine, and peak integration. A secondary script was used for spectral deconvolution and individual integration of non-resolved peaks by fitting them to theoretical Lorentzian curves. Relative concentrations of the components of the binary mixtures were calculated using theformula:

$$\%component\,"x" = \frac{I_x}{I_x + I_y} \times 100\#$$

where I_x and I_y are the values of the integral for peaks corresponding to methyl groups from each component of the binary mixture based on the processed NMR spectrum.

2.6. Hazards

All the phthalate diesters were liquid at room temperature. Phthalate diesters are classified as endocrine-disrupting chemicals that can interfere with normal hormonal signaling and potentially cause hormonal imbalances and reproductive toxicity. [1,3,7,8,9] The health risksassociated with phthalate diesters are dependent on their structure, alkyl chain length, concentration, and duration of exposure. [1,2,3,6]. Therefore, all normal laboratory safety protocolsincluding proper use of personal protective equipment were followed to minimize contact with harmful material.

3. Results and Discussion

3.1. Gas Chromatography – Flame Ionization Detection

GC chromatograms of the four phthalate standards showed fully resolved peaks, shown in Figure 3, allowing precise identification of each individual reference standard. Retention time for dimethyl phthalate was approximately 7.0 mins, for diethyl phthalate 9.3 mins, for dipropyl phthalate 12.8 mins, and for dibutyl phthalate 16.2 mins.

Retentiontime on the nonpolar column is primarily driven by differences in alkyl chain length, molecular weight, and boiling point. From methyl (C1) to butyl (C4), as molecular weight and boiling point increases, the sample retention time also increases. Stacked GC chromatograms of binary mixtures also show that peak intensities change proportionally with varying mixture composition ratios, as shown by the stacked spectra for the DMP:DEP series of mixtures in Figure 4. Retention times for materials in mixtures remain constant with those of the standard samples, as expected. Peak intensities for DMP and DEP in binary mixtures are inversely proportional.

This inverse relationship is consistent with the relative proportions of the compounds in binary mixtures, allowing quantifiable and distinguishable peaks for comparing ratios.

The retention times of the four phthalate diester standards were adequately resolved, allowing straightforward quantification of relative phthalate diester concentrations in binary mixtures. Quantitative analysis was performed by integrating peak areas for each binary mixture, using them to calculate an experimental component ratio (as shown in equation 2), and comparing them to known gravimetric values as shown in Figure 5. The resulting plots showed strong linear relationships between calculated and actual weighted percentages, with regression coefficients of R^2= 0.9292 for both DMP and DEP.

Similar linear relationships between calculated and actual weight percentages were observed for all other binary phthalate diester mixtures as shown in Figure 6, Figure 7, Figure 8, Figure 9 and Figure 10, demonstrating consistent quantification of relative phthalate diester concentrations compared to known gravimetric weight percentages.

Compound-specific response factors were not applied in this study; therefore, GC-FID peak-height ratios were interpreted as relative compositional estimates rather than fully corrected absolute weight-percent values. Future work should include response-factor correction or compound-specific calibration curves to improve quantitative accuracy.

Limits of detection (LOD) and limits of quantification (LOQ) were not determined in this study. Because the primary objective was to compare the compositional analysis of gravimetrically prepared binary mixtures, the work focused on linear relationships between analytical response and known mixture composition rather than trace-level detection sensitivity.

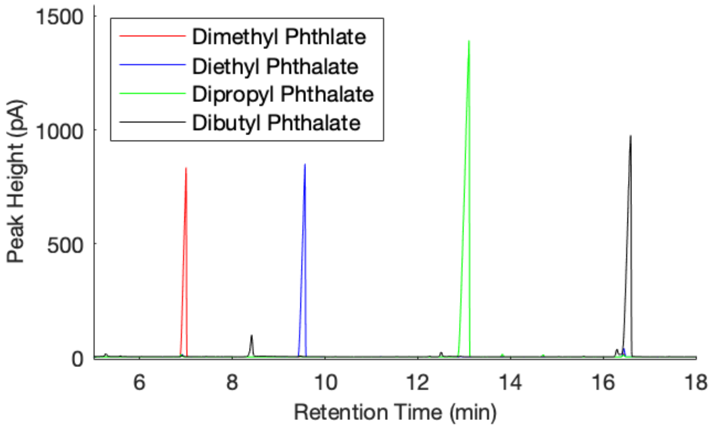

Figure 3. Gas Chromatograms of four phthalate standards: GC–FID chromatogram showing the retention times and peak intensities of the four individual phthalate diester standards analyzed. The compounds and their corresponding peaks are: dimethyl phthalate (red, ~7.0 min), diethyl phthalate (blue, ~9.3 min), dipropyl phthalate (green, ~12.8 min), and dibutyl phthalate (black, ~16.2 min)

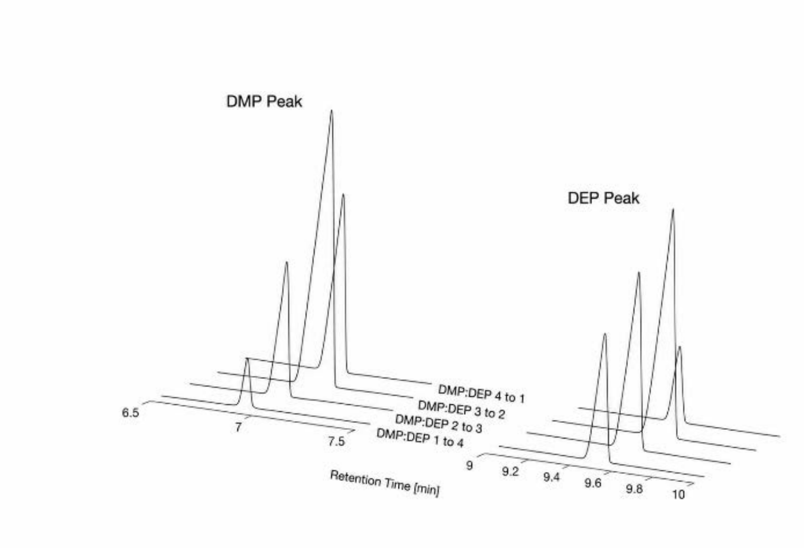

Figure 4. Stacked GC chromatograms showing DMP and DEP peaks across DMP:DEP mixtures (1:4, 2:3, 3:2, 4:1). Peak intensities change proportionally with mixture composition, allowing clear differentiation and quantification of DMP and DEP

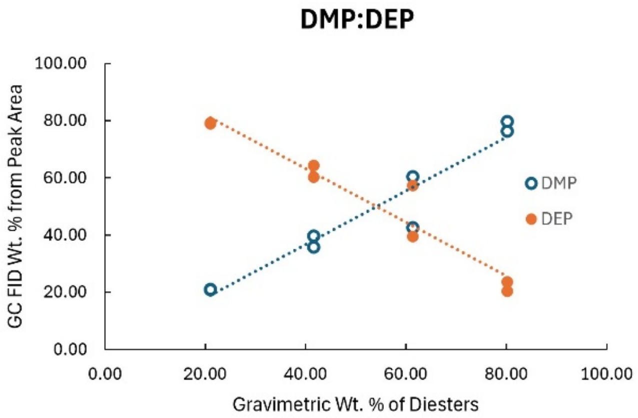

Figure 5. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DMP (blue) and DEP (orange) in DMP: DEP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.0094x - 0.0072$, $R^2 = 0.9292$) and DEP ($y = -0.0094x + 1.0072$, $R^2 = 0.9292$) for combined data; DMP ($y = 0.01x - 0.0087$, $R^2 = 0.9991$) and DEP ($y = -0.01x + 1.0087$, $R^2 = 0.9991$) for data set 1; DMP ($y = 0.9528x - 0.0087$, $R^2 = 0.9924$) and DEP ($y = -0.9528x + 1.0087$, $R^2 = 0.9924$) for data set 2

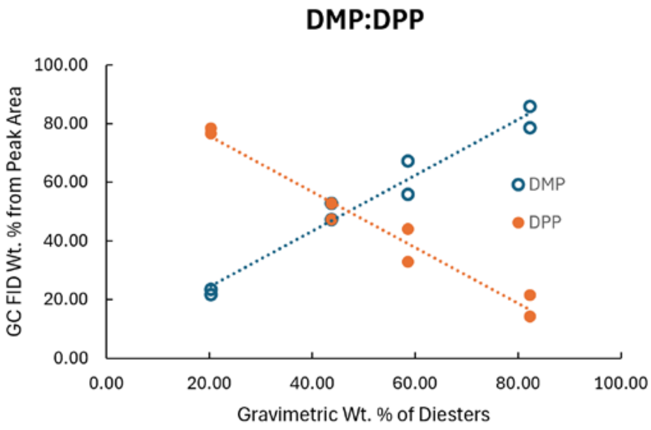

Figure 6. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DMP (blue) and DPP (orange) in DMP: DEP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.0095x + 0.0528$, $R^2 = 0.9638$) and DPP ($y = -0.0095x + 0.9472$, $R^2 = 0.9638$) for combined data; DMP ($y = 0.0103x + 0.0404$, $R^2 = 0.9813$) and DPP ($y = -0.0103x + 0.9596$, $R^2 = 0.9813$) for data set 1; DMP ($y = 0.8736x + 0.0652$, $R^2 = 0.9935$) and DPP ($y = -0.8736x + 0.9348$, $R^2 = 0.9935$ for data set 2

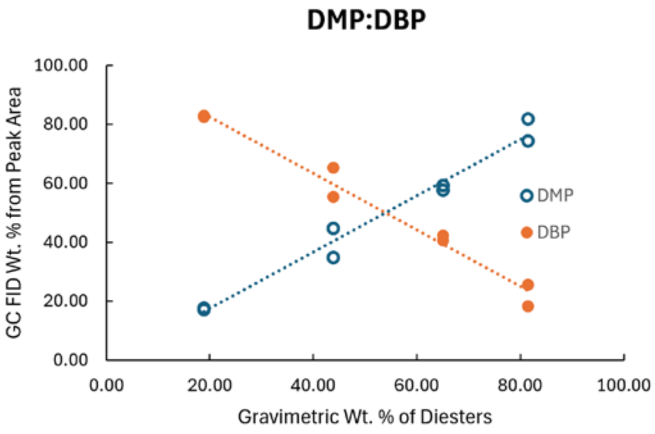

Figure 7. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DMP (blue) and DBP (orange) in DMP: DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.0096x - 0.0153$, $R^2 = 0.977$) and DBP ($y = -0.0096x + 1.0153$, $R^2 = 0.977$) for combined data; DMP $y = 0.0098x - 0.0065$, $R^2 = 0.9809$) and DBP ($y = -0.0098x + 1.0065$, $R^2 = 0.9809$) for data set 1; DMP ($y = 0.9333x - 0.0242$, $R^2 = 0.9902$) and DBP ($y = -0.9333x + 1.0242$, $R^2 = 0.9902$ for data set 2

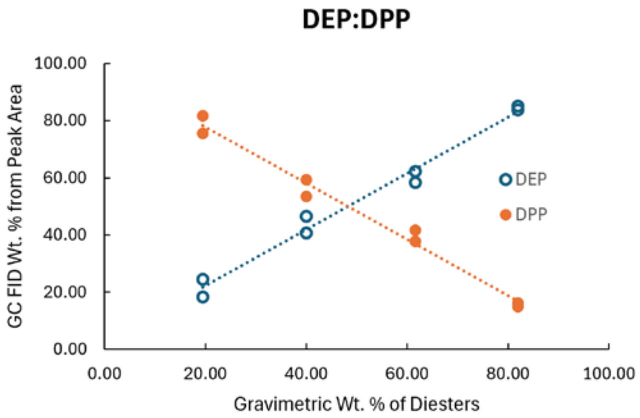

Figure 8. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DEP (blue) and DPP (orange) in DMP: DPP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP ($y = 0.0098x + 0.0254$, $R^2 = 0.9835$) and DPP ($y = -0.0098x + 0.9746$, $R^2 = 0.9835$) for combined data; DEP ($y = 0.009x + 0.0734$, $R^2 = 0.9796$); DPP ($y = -0.009x + 0.9266$, $R^2 = 0.9796$) for data set 1, DEP ($y = 1.0608x - 0.0226$, $R^2 = 0.9995$) and DPP ($y = -1.0608x + 1.0226$, $R^2 = 0.9995$ for data set 2

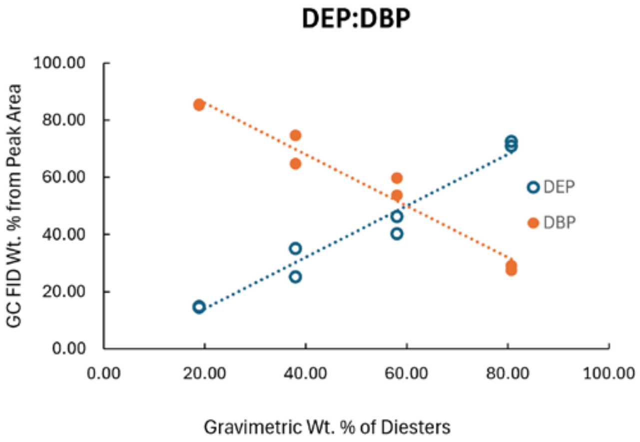

Figure 9. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DEP (blue) and DBP (orange) in DEP: DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP ($y = 0.009x - 0.0401$, $R^2 = 0.96$) and DBP ($y = -0.009x + 1.0401$, $R^2 = 0.96$) for combined data; DEP ($y = 0.009x - 0.0635$, $R^2 = 0.9587$) and DBP ($y = -0.009x + 1.0635$, $R^2 = 0.9587$) for data set 1; DEP ($y = 0.8982x - 0.0167$, $R^2 = 0.9834$) and DBP ($y = -0.8982x + 1.0167$, $R^2 = 0.9834$ for data set 2

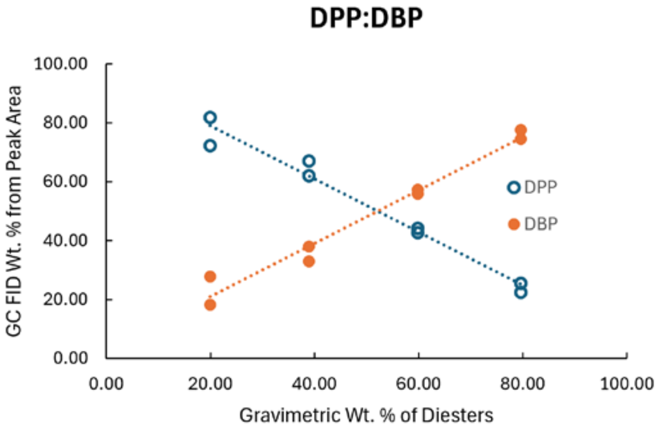

Figure 10. GC-FID-determined calculated weight percent composition, determined from relative peak integrations, plotted against gravimetric weight percent for DPP (blue) and DBP (orange) in DPP: DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DPP ($y = 0.009x + 0.0294$, $R^2 = 0.9734$) and DBP ($y = -0.009x + 0.9706$, $R^2 = 0.9734$) for combined data; DBP ($y = 0.0101x - 0.0383$, $R^2 = 0.9944$) and DPP ($y = -0.0101x + 1.0383$, $R^2 = 0.9944$) for data set 1; DBP ($y = 0.7997x + 0.0972$, $R^2 = 0.9896$) and DPP ($y = -0.7997x + 0.9028$, $R^2 = 0.9896$ for data set 2

3.2. Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)

Each pure phthalate diester standard exhibited distinct sets of resonance frequencies for DMP, DEP, DPP, and DBP as shown in Figure 11. Each phthalate diester is unique in the length of the alkyl group attached to the terminal oxygen of its ester group. Each additional CH$_2$ has its own resonance frequency, allowing for differentiation. The peaks analyzed for this study corresponded to the terminal methyl groups of each compound, found at ~3.8 ppm (DMP), ~1.2 ppm (DEP), ~0.83 ppm (DPP), and ~0.85 ppm (DBP).

The terminal methyl group of each phthalate diester served as a strong quantification tool because they are relatively easy to isolate. For example, the methyl resonance of DMP (≈3.8 ppm) and DBP (≈0.85 ppm) are well resolved in all mixture ratios as shown in Figure 12. This allowed straightforward peak integration and comparison across all four binary mixtures. Figure 12 shows that the relative integrations of these peaks change proportionally with the known mixture composition as expected.

In cases where proton resonances overlapped, MATLAB-based spectral deconvolution was successfully applied to resolve individual peaks and extract reliable integration values. The strong linear correlation (R^2 = 0.9991) between gravimetrically determined weight percentages and NMR-derived concentrations confirms that ^{1}H NMR is an analytical tool for analysis of this mixture as shown in Figure 13.

Similar linear correlations were observed for other binary mixtures (Figure 14, Figure 15, Figure 16, Figure 17), indicating consistent results in NMR-derived concentrations compared to their known gravimetric weight percentages.

A limitation of the ^{1}H NMR method was observed for the DPP/DBP binary mixture. Due to the close structural similarity of the propyl and butyl alkyl chains, several proton signals overlapped and could not be reliably resolved or integrated for quantitative analysis.

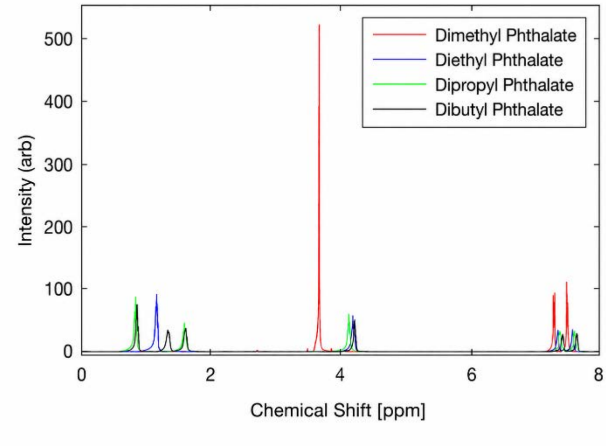

Figure 11. ^{1}H NMR Spectra of Phthalate Standards: ^{1}H NMR spectra of dimethyl (red), diethyl (blue), dipropyl (green), and dibutyl (black) phthalate standards. The peaks analyzed for this study were those corresponding to the methyl groups of each compound, found at ~3.8 ppm (DMP), ~1.2 ppm (DEP), ~0.83 ppm (DPP) and ~0.85 ppm (DBP)

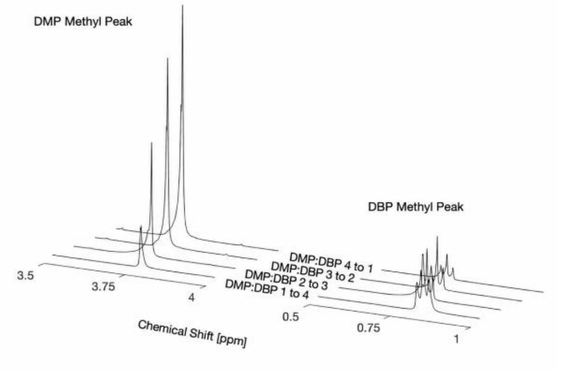

Figure 12. Comparison of ^{1}H NMR Methyl Peak of Dimethyl and Dibutyl Phthalates: Stacked ^{1}H NMR spectra of binary mixtures of dimethyl (DMP) and dibutyl (DBP) phthalate showing the methyl resonance regions from for the DMP methyl peak (3.68 ppm) and DBP methyl peak (0.83 ppm) vary as mixture composition changes gradually from 1:4 to 4:1

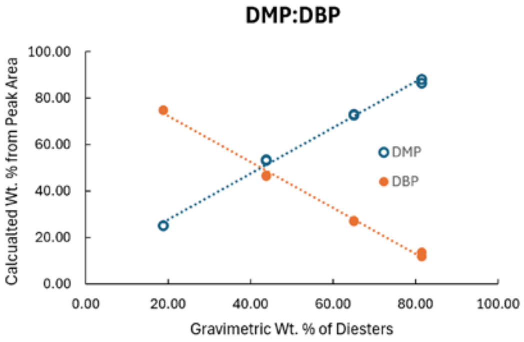

Figure 13. ^{1}H NMR-determined calculated weight percent composition, determined from relative integration of diagnostic methyl resonances, plotted against gravimetric weight percent for DMP (blue) and DBP (orange) in DMP:DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.9888x + 7.9732$, $R^2 = 0.9958$) and DBP ($y = -0.9888x + 92.027$, $R^2 = 0.9958$) for combined data; DMP ($y = 0.072x - 0.4972$, $R^2 = 0.9935$) and DBP ($y = -0.0314x + 3.5102$, $R^2 = 0.9843$) for data set 1; DMP ($y = 1.0001x + 7.7664$, $R^2 = 0.9968$) and DBP ($y = 1.0001x + 92.324$, $R^2 = 0.9968$ for data set 2

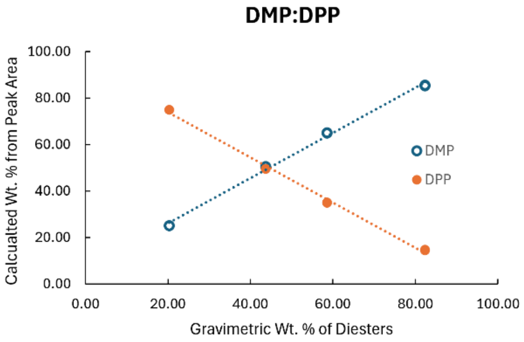

Figure 14. ^{1}H NMR-determined calculated weight percent composition, determined from relative integration of diagnostic methyl resonances, plotted against gravimetric weight percent for DMP (blue) and DPP (orange) in DMP: DPP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.9738x + 6.6345$, $R^2 = 0.9964$) and DPP ($y = -0.9738x + 93.366$, $R^2 = 0.9964$) for combined data; DMP ($y = 0.072x - 0.3952$, $R^2 = 0.9928$) and DPP ($y = -0.0418x + 4.4066$, $R^2 = 0.9994$) for data set 1; DMP ($y = 0.9723x + 6.6571$, $R^2 = 0.9963$) and DPP ($y = -0.9723x + 93.343$, $R^2 = 0.9963$ for data set 2

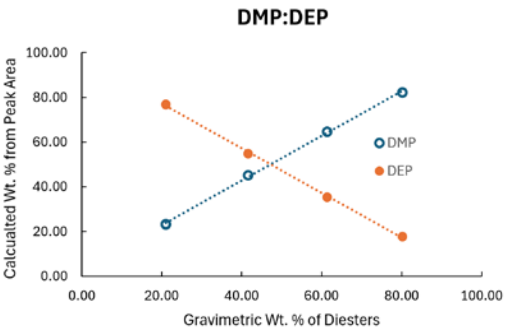

Figure 15. ¹H NMR-determined calculated weight percent composition, determined from relative integration of diagnostic methyl resonances, plotted against gravimetric weight percent for DMP (blue) and DEP (orange) in DMP: DEP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.9982x + 2.8481$, $R^2 = 0.9991$) and DEP ($y = -0.9982x + 97.152$, $R^2 = 0.9991$) for combined data; DMP ($y = 0.9945x + 3.0765$, $R^2 = 0.9991$) and DEP ($y = -0.9945x + 96.924$, $R^2 = 0.9991$) for data set 1; DMP ($y = 1.002x + 2.6197$, $R^2 = 0.9991$) and DEP ($y = -1.002x + 97.38$, $R^2 = 0.9991$ for data set 2

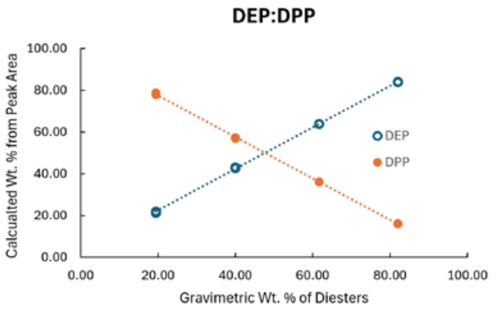

Figure 16. ¹H NMR-determined calculated weight percent composition, determined from relative integration of diagnostic methyl resonances, plotted against gravimetric weight percent for DEP (blue) and DPP (orange) in DEP:DPP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP ($y = 0.9946x + 2.5736$, $R^2 = 0.9997$) and DEP ($y = -0.9946x + 2.5736$, $R^2 = 0.9997$) for combined data; DEP ($y = 0.0411x + 0.1055$, $R^2 = 0.9929$) and DPP ($y = -0.0413x + 4.018$, $R^2 = 0.9986$) for data set 1, DEP ($y = 0.9985x + 2.1276$, $R^2 = 0.9998$) and DPP ($y = -0.9985x + 97.872$, $R^2 = 0.9998$ for data set 2

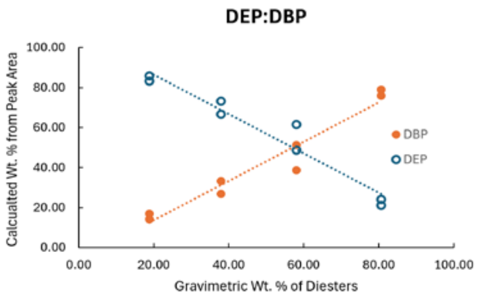

Figure 17. ¹H NMR-determined calculated weight percent composition, determined from relative integration of diagnostic methyl resonances, plotted against gravimetric weight percent for DEP (blue) and DBP (orange) in DEP:DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP ($y = 0.9829x - 6.0535$, $R^2 = 0.9447$) and DBP ($y = -0.9829x + 106.05$, $R^2 = 0.9447$) for combined data; DEP ($y = -0.225x + 58.804$, $R^2 = 0.9769$) and DBP ($y = 0.225x + 41.496$, $R^2 = 0.9769$) for data set 1; DEP ($y = -0.9522x + 102.18$, $R^2 = 0.9967$) and DBP ($y = 0.9522x - 2.1812$, $R^2 = 0.9967$ for data set 2

3.3. FTIR Spectroscopy (FTIR-ATR)

FTIR-ATR spectroscopy further complemented GC-FID and NMR by providing characteristic absorbance bands for each phthalate diester. All compounds displayed common absorptions expected for aromatic phthalate diesters, including aromatic C–H stretching vibrations near 3100–3000 cm⁻¹, aliphatic sp^3 C–H stretching bands near 2960–2850 cm⁻¹, a strong ester carbonyl (C=O) stretch near 1730–1715 cm⁻¹, aromatic C=C stretching bands near 1600–1500 cm⁻¹, and ester C–O stretching absorptions in the 1280–1120 cm⁻¹ region. Additional bands in the fingerprint region, including aromatic C–H out-of-plane bending and alkyl-related bending vibrations, helped distinguish the individual phthalate diesters. Although the spectra were broadly similar because all four compounds shared the same phthalate aromatic diester core, differences in the alkyl-related absorptions became useful for differentiation as chain length increased.

FTIR spectra of the four pure phthalates showed clear differences were observed in the fingerprint region (400-1500 cm⁻¹), where subtle variations in alkyl chain structure produced unique distinct absorptions, as shown in Figure 18. Dimethyl phthalate had a uniquepeak at 1434 cm⁻¹, diethyl phthalate at 1366 cm⁻¹, dipropyl phthalate at 914 cm⁻¹, and dibutyl phthalate at 502 cm⁻¹. These peaks provided useful markers for distinguishing the standards. Since the aromatic diester part of the molecule remains the same across the four compounds, the spectral differences are due to the alkyl chain length and result in unique identifiers in the fingerprint region due to unique stretching vibrations of the C-H bond.

Spectra of DMP:DEP mixtures were examined in the narrow regions surrounding the peaks for dimethyl phthalate and diethyl phthalate, as shown in Figure 19. In the 1410-1450 cm⁻¹ region, the DMP band changed in intensity as the DMP composition changed, and in the 1340-1380 cm⁻¹ region, the DEP band showed the opposite trend. As the proportion of one component increased, its corresponding absorption became more pronounced, while the peak of another component decreased. This represents an inverse relationship, indicating that relative peak heights can be used to monitor the relative composition of a binary mixture.

A quantitative analysis was performed using relative peak heights to calculate the percent composition of DMP and DEP in binary mixtures, and these values were compared with known gravimetric weight percentages as shown in Figure 2. The resulting plots show a strong linear relationship. For DMP, the regression had and $R^2 = 0.9889$, and for DEP, the $R^2$was the same. These strong linear relationships suggest FTIR peak-height analysis is a reliable technique for measuring the mixture composition across a range of concentration ratios. The inverse slopes of the two regressions are expected, since increasing the proportion of DMP decreases the proportion of DEP relative to the gravimetrically prepared samples.

The resulting plots for the remaining binary mixtures also showed strong linear relationships (Figure 21, Figure 22, Figure 23, Figure 24, Figure 25), supporting the use of FTIR peak-height analyses to measure mixture composition.

FTIR was a useful spectroscopy technique for both qualitative and quantitative analysis of phthalate diesters. The standard could be differentiated through unique bands in the fingerprint region, while the binary mixtures could be analyzed and quantified through compositional changes in relative peak heights. Although FTIR does not separate compounds as GC does, the high correlation coefficient observed for DMP:DEP mixtures demonstrates that it can still be used as an effective spectroscopic technique for obtaining compositional information about binary mixtures.

Although all FTIR regressions showed strong linear correlations based on R² values, all regressions produced large intercepts, indicating that the raw peak-height ratios cannot directly correspond to the true gravimetric composition without calibration. Therefore, these FTIR relationships should be interpreted as calibration-based models rather than direct 1:1 composition measurements.

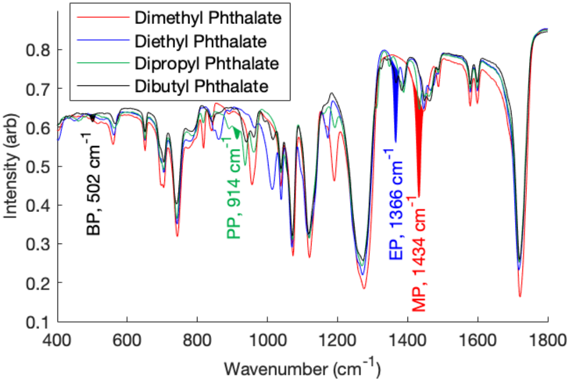

Figure 18. FTIR Spectra of Phthalate Standards: FTIR spectra of pure dimethyl (red), diethyl (blue), dipropyl (green), and dibutyl (black) phthalate standards highlighting differences within the fingerprint region (400–1500 cm⁻¹). Distinct diagnostic bands are labeled for each compound: DBP (502 cm⁻¹), DPP (914 cm⁻¹), DEP (1366 cm⁻¹), and DMP (1434 cm⁻¹)

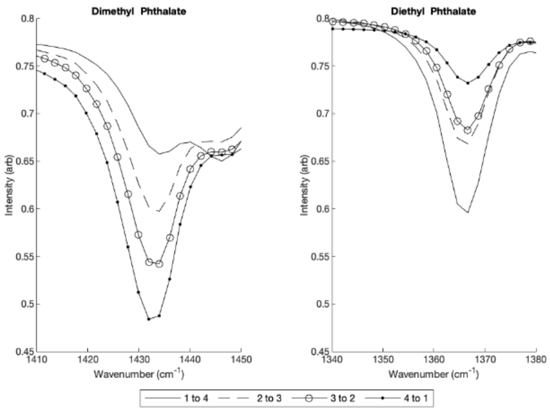

Figure 19. FTIR Spectra for Dimethyl-Diethyl Phthalate Mixtures: Zoomed FTIR spectra comparing the 1410–1450 cm⁻¹ (Dimethyl Phthalate, left) and 1340-1380 cm⁻⁻¹ (Diethyl Phthalate, right) regions across binary mixture ratios (1:4 [solid line], 2:3 [dashed line], 3:2 [solid line with circles], 4:1 [solid line with dots])

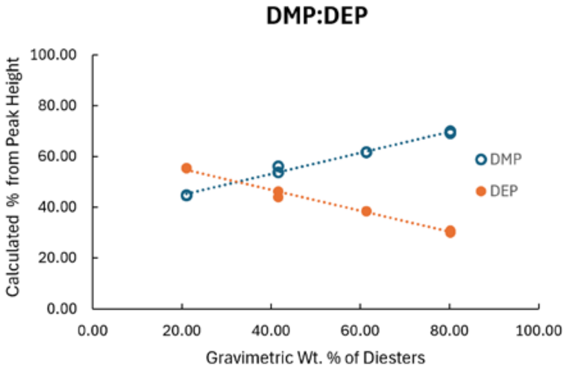

Figure 20. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DMP (blue) and DEP (orange) in DMP:DEP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP ($y = 0.4127x + 36.607$, $R^2 = 0.9899$) and DEP ($y = -0.4127x + 63.393$, $R^2 = 0.9899$) for combined data; DMP ($y = 0.4116x + 37.087$, $R^2 = 0.9846$) and DEP ($y = -0.4116x + 62.913$, $R^2 = 0.9846$) for data set 1; DMP ($y = 0.4139x + 36.128$, $R^2 = 0.9994$) and DEP ($y = -0.4139x + 63.872$, $R^2 = 0.9994$) data set 2

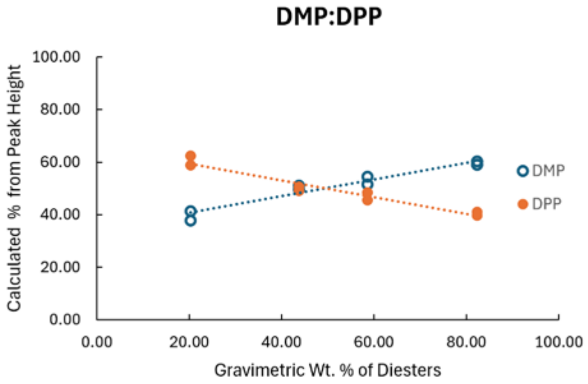

Figure 21. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DMP (blue) and DPP (orange) in DMP:DPP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP (y = 0.3176x + 34.307, R² = 0.9414) and DPP (y = −0.3176x + 65.693, R² = 0.9414) for combined data; DMP (y = 0.3075x + 35.608, R² = 0.9913) and DPP (y = −0.3075x + 64.392, R² = 0.9913) for data set 1; DMP (y = 0.2573x + 36.034, R² = 0.9698) and DPP (y = -0.2573x + 63.966, R² = 0.9698) data set 2

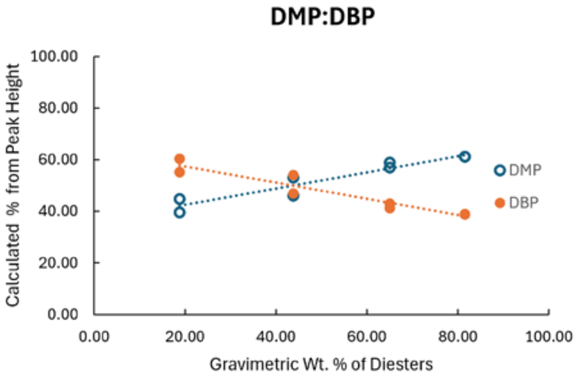

Figure 22. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DMP (blue) and DBP (orange) in DMP:DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DMP (y = 0.3131x + 36.326, R² = 0.907) and DPP (y = −0.3131x + 63.674, R² = 0.907) for combined data; DMP (y = 0.3075x + 35.608, R² = 0.9913) and DPP (y = −0.3075x + 64.392, R² = 0.9913) for data set 1; DMP (y = 0.3711x + 31.994, R² = 0.9557) and DBP (y = -0.3711x + 68.006, R² = 0.9557) data set 2

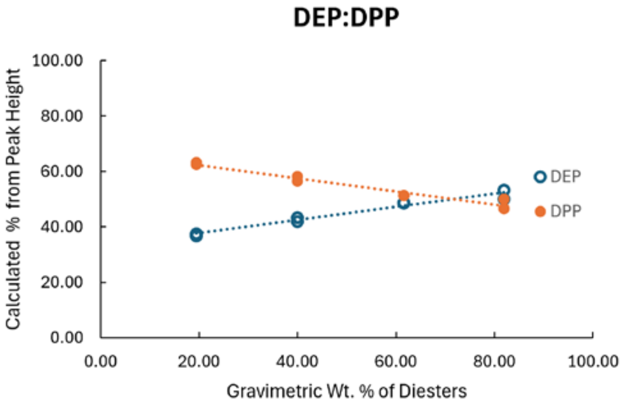

Figure 23. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DEP (blue) and DPP (orange) in DEP:DPP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP (y = 0.2367x + 33.019, R² = 0.9571) and DPP (y = −0.2367x + 66.981, R² = 0.9571for combined data; DEP (y = 0.2825x + 31.06, R² = 0.9962) and DPP (y = −0.2825x + 68.94, R² = 0.9962) for data set ; DEP (y = 0.2514x + 32.962, R² = 0.9972) and DPP (y = -0.2514x + 67.038, R² = 0.9972) data set 2

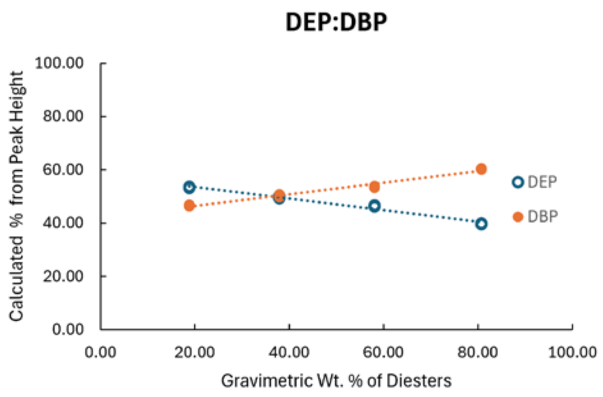

Figure 24. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DEP (blue) and DBP (orange) in DEP:DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DEP ($y = 0.2182x + 42.019$, $R^2 = 0.9786$) and DBP ($y = -0.2182x + 57.981$, $R^2 = 0.9786$) for combined data; DEP ($y = -0.225x + 58.504$, $R^2 = 0.9769$) and DBP ($y = 0.225x + 41.496$, $R^2 = 0.9769$) for data set 1; DEP ($y = -0.2114x + 57.458$, $R^2 = 0.9856$) and DBP ($y = 0.2114x + 42.542$, $R^2 = 0.9856$) data set 2

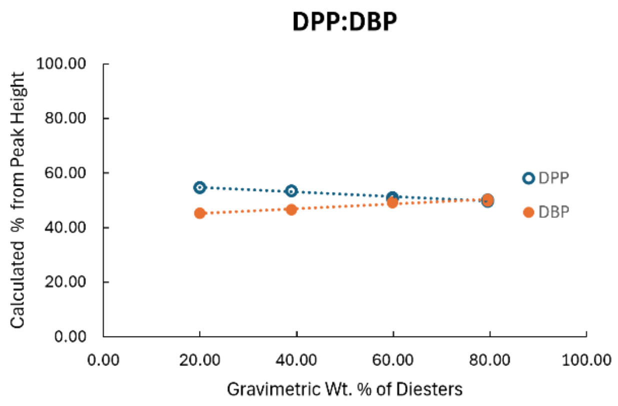

Figure 25. FTIR-determined calculated weight percent composition, determined from relative peak heights, plotted against gravimetric weight percent for DPP (blue) and DBP (orange) in DEP: DBP binary mixtures. Each composition was analyzed in duplicate trials; overlapping points indicate superimposed values. Linear regression equations are: DPP ($y = 0.0851x + 43.56$, $R^2 = 0.9559$) and DBP ($y = -0.0851x + 56.44$, $R^2 = 0.9559$) for combined data; DBP ($y = 0.1071x + 42.782$, $R^2 = 0.9629$) and DPP ($y = -0.1071x + 57.218$, $R^2 = 0.9629$) for data set 1; DPP ($y = -0.0771x + 56.125$, $R^2 = 0.9660$) and DBP ($y = 0.0771x + 43.875$, $R^2 = 0.9660$) data set 2

3.4. General Discussion

The compositional analysis of pure short-chain phthalate diesters (DMP, DEP, DPP, and DBP) and their binary mixtures presents a unique challenge due to their close structural similarity. These compounds share a common phthalate diester structure and differ only in the length of their alkyl chains, making their compound-specific identification difficult. This study demonstrates that a multi-instrumental analytical approach, including GC-FID, ^{1}H NMR spectroscopy, and FTIR-ATR spectroscopy, can effectively discover subtle structural differences to achieve reliable compositional analysis. In general, excellent precision of all the experimental data was supported by results obtained from analyst 1 and analyst 2. Analysis of the composite data revealed no significant variance, supported by correlation coefficients consistently above 0.9. When applied together, these techniques confirm the reliability of spectroscopic and chromatographic methods for the identification and quantification of these short-chain alkyl phthalate diesters.

Therefore, the methods evaluated here are not intended to directly represent trace-level detection in water, food, medical products, or other real-world samples. Instead, this work focuses on determining whether GC-FID, FTIR-ATR, and ^{1}H NMR spectroscopy can distinguish and quantify structurally similar short-chain phthalate diesters under controlled mixture conditions. Application of these methods to environmental or consumer-product samples would require additional method development, including matrix-matched standards, sample extraction or preconcentration steps, detection limit studies, and evaluation of more complex mixtures containing three or more phthalate components.

3.5. Method Comparison and Reliability

Overall, comparing the three methods showed that each technique provided useful information in a slightly different way, and together they gave more reliable results than any single method alone. GC was effective for separating the binary mixture and precisely measuring how much of each phthalate diester was present, since it produced clearly separated peaks that were easy to quantify. NMR was especially useful for identifying each compound based on its molecular structure and also allowed for accurate quantification by measuring signal intensities, even when some signals overlapped. FTIR did not separate the compounds like GC, but it helped confirm their chemical identity based on their characteristic bond vibration frequencies and supported the other techniques through spectral analysis. Because all three methods produced results that closely matched the gravimetrically prepared compositions, this comparison shows that using multiple complementary techniques increases confidence in the accuracy and reliability of the measurements.

4. Conclusion

^{1}H NMR spectra displayed distinct alkyl proton resonances for each phthalate diester, allowing for differentiation between compounds based on chemical shifts and splitting patterns. Spectral deconvolution was applied to overlapping peaks. FTIR spectra exhibited unique absorbance bands in the fingerprint region for the four pure phthalate diesters, enabling compound identification. GC-FID generated fully resolved chromatograms for all samples, with clearly distinguishable retention times for each phthalate diester. Integrated peak areas from the NMR spectra and GC chromatograms, and peak intensities from FTIR spectra were used to calculate the relative concentrations of dimethyl, diethyl, dipropyl, and dibutyl phthalates in binary mixtures with a high degree of accuracy. The combined analytical approach demonstrated that ^{1}H NMR, FTIR-ATR, and GC-FID can accurately quantify phthalate diesters when present in binary mixtures simultaneously. Overall, these results confirm the reliability of spectroscopic and chromatographic methods for the identification and quantification of these short-chain alkyl phthalate diesters.

From an applied perspective, the ability to accurately quantify short-chain phthalates in mixtures is particularly important due to their environmental and health implications. Lower molecular weight phthalates, such as DMP, are more prone to leaching from polymers into surrounding environments compared to higher molecular weight phthalate diesters like DBP. Given their classification as endocrine-disrupting chemicals, precise quantification of these compounds in consumer products and environmental samples is essential for assessing potential human exposure and reproductive toxicity.

ACKNOWLEDGEMENTS

We acknowledge financial support from a Hofstra HCLAS faculty research & Development Grant awarded to Dr. R. P. D’ Amelia, and a startup fund provided to Dr. M. T. Rooney by Hofstra University. MATLAB R2025 scripts weredeveloped in house by Dr. M. T. Rooney (Department of Chemistry, Hofstra University).

List of Abbreviations and Symbols:

DMP = dimethyl phthalate
DEP = diethyl phthalate
DPP = dipropyl phthalate
DBP = dibutyl phthalate
NMR = nuclear magnetic resonance spectroscopy
1H NMR = proton nuclear magnetic resonance spectroscopy
FTIR = Fourier-transform infrared spectroscopy
GC-FID = gas chromatography – flame ionization detection
ATR = attenuated total reflectance

References

[1] Mankidy, R., Wiseman, S., Ma, H. and Giesy, J. P. (2013) Biological impact of phthalates. Toxicol. Lett.217, 50-58.

[2] Net, S., Sempéré, R., Delmont, A., Paluselli, A. and Ouddane, B. (2015) Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ. Sci. Technol.49, 4019-4035.

[3] Wang, Y. and Qian, H. (2021, May 1) Phthalates and their impacts on human health. Healthcare (Switzerland), MDPI AG.

[4] Alak, G., Köktürk, M. and Atamanalp, M. (2024) Evaluation of phthalate migration potential in vacuum-packed. Sci. Rep., Nature Research 14.

[5] Liu, J., Li, C., Yang, F., Zhao, N., Lv, S., Liu, J., et al. (2020) Assessment of migration regularity of phthalates from food packaging materials. Food Sci. Nutr.8, 5738-5747.

[6] Lee, Y.-M., Lim, Y., Kang, S. and Kim, S. (2025) Migration of phthalate and non-phthalate plasticizers from polyvinyl chloride (PVC) materials. Sci. Total Environ.1002, 180559.

[7] Moghazy, M., Papathanasiou, M., Tzoupis, H., Papavasileiou, K. D., Xing, C., Lauschke, V. M., et al. (2025, September 1) A Systematic Literature Review of Reproductive Toxicological Studies on Phthalates. Int. J. Mol. Sci., Multidisciplinary Digital Publishing Institute (MDPI) .

[8] Hlisníková, H., Petrovičová, I., Kolena, B., Šidlovská, M. and Sirotkin, A. (2020, September 1) Effects and mechanisms of phthalates’ action on reproductive processes and reproductive health: A literature review. Int. J. Environ. Res. Public Health, MDPI AG.

[9] Sedha, S., Lee, H., Singh, S., Kumar, S., Jain, S., Ahmad, A., et al. (2021) Reproductive toxic potential of phthalate compounds - State of art review. Pharmacol. Res.167, 105536.

[10] Wang, J., Weng, X., Liu, S., Zhang, H., Zhu, Q., Fu, Q., et al. (2023, November 17) Occurrence, Fate, and Reduction Measures of Phthalates in the Cooking Process: A Review. Environment and Health, American Chemical Society.

[11] Bhogal, S., Grover, A. and Mohiuddin, I. (2024) A Review of the Analysis of Phthalates by Gas Chromatography in Aqueous and Food Matrices. Crit. Rev. Anal. Chem.54, 3428-3452.

[12] Yan, H., Liu, B., Du, J. and Row, K. H. (2010) Simultaneous determination of four phthalate esters in bottled water using ultrasound-assisted dispersive liquid-liquid microextraction followed by GC-FID detection. Analyst135, 2585.

[13] Freitas, F., Cabrita, M. J. and da Silva, M. G. (2023, November 1) A Critical Review of Analytical Methods for the Quantification of Phthalates Esters in Two Important European Food Products: Olive Oil and Wine. Molecules, Multidisciplinary Digital Publishing Institute (MDPI).

[14] P. D’Amelia, R. and H. Kreth, E. (2024) Application of Molecular Spectroscopies for the Compositional Analysis of Short Chain Cinnamyl Ester Mixtures. World Journal of Analytical Chemistry, Science and Education Publishing Co., Ltd. 9, 1-9.

[15] D’Amelia, R. P. and Khanyan, B. (2022) Compositional Analysis of Mixtures of Oleate Esters of Short Chain Alcohols (C1-C4) by Quantitative Proton Nuclear Magnetic Resonance Spectroscopy (qPNMR). World Journal of Chemical Education, Science and Education Publishing Co. Ltd 10, 1-7.

[16] D’Amelia, R. P., Kimura, M. W. and Nirode, W. F. (2021) Application of Quantitative Proton Nuclear Magnetic Resonance Spectroscopy for the Compositional Analysis of Short-Chain Fatty Acid Ethyl Ester Mixtures. World Journal of Chemical Education, Science and Education Publishing Co. Ltd 9, 8-13.

[17] P. D’Amelia, Ronald., Huang, L., F. Nirode, W., Rotman, E.,

Shumila, J. and M. Wachter, N. (2015) Application of ¹H-NMR for the Quantitative Analysis of Short Chain Fatty Acid Methyl Ester Mixtures: An Undergraduate Instrumental Analysis Experiment. World Journal of Chemical Education, Science and Education Publishing Co., Ltd. 3, 46-50.

[18] D’Amelia, R. P., Mancuso, J. and Wachter, N. (2019) Application of Quantitative Proton Nuclear Magnetic Resonance Spectroscopy for the Compositional Analysis of Short Chain Fatty Acid Benzyl Ester Mixtures. World Journal of Chemical Education, Science and Education Publishing Co. Ltd 7, 189-195.

[19] P. D’Amelia, R., W. Kimura, M. and Villon, M.-C. (2021) Qualitative and Quantitative Analyses of Synthesized Short-Chain Fatty Acid Phenyl Esters Using Fourier-Transform Infrared Spectroscopy. World Journal of Organic Chemistry, Science and Education Publishing Co., Ltd. 9, 6-17.

[20] P. D’Amelia, R., W. Kimura, M. and F. Nirode, W. (2020) Application of Quantitative Proton Nuclear Magnetic Resonance Spectroscopy for the Compositional Analysis of Short-Chain Fatty Acid Ethyl Ester Mixtures. World Journal of Chemical Education8, 170−175.