

Advancements in Petroleum Fractionation: Overcoming Challenges and Enhancing Efficiency

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Introduction

Extractable petroleum hydrocarbon (EPH) fractionation is a specialized methodology utilized to separate the aliphatic and aromatic fractions of petroleum hydrocarbons found in environmental samples. This testing is a subset of Total Petroleum Hydrocarbons (TPH) which are measurable amounts of petroleum-based chemicals in gasoline, diesel, and oil range organics. Information obtained from EPH fractionation testing provides a more detailed assessment of the hydrocarbon composition and helps environmental scientists identify the potential impact of these contaminants. Three laboratory techniques commonly used for EPH fractionation are: High-Performance Liquid Chromatography (HPLC) Fractionation, Gas Chromatography with a secondary column (GCxGC-FID), and Solid Phase Extraction (SPE). Each technique has challenges such as low sample throughput, high solvent usage, breakthrough of fractions, potential contamination, and issues related to analytical data processing. This presentation outlines challenges for SPE and solutions to meet the regulatory requirements of various regions in North America.

Step 1: Extraction

The traditional EPH workflow employs the use of large separatory funnels and copious amounts of solvent to isolate and extract the hydrocarbons from the soil and/or water samples. The Two-Step approach with the Biotage® workflow solution, demonstrated in Fig 1, reduces solvent consumption and sample preparation time.



Fig 1. EPH Workflow: Step 1 - Extraction.

Step 2: Fractionation

Table 1 compares three common techniques for EPH Fractionation. Several factors were considered and whereas GCxGC-FID does not consume high amounts of solvent, efficiency is lost due to the length of time for fractionation. The best overall approach is Automated SPE combined with GC-FID. Solvent and time are reduced when processing samples with this approach, increasing workflow efficiency in the laboratory.

	HPLC Fractionation & GC-FID	GCxGC-FID	Automated SPE & GC-FID
Fractionation Time (hr)	8	12	1
Analysis Time (hr)	6	12	6
Total Processing Time (hr)	14	12	7
Total Solvent Use (mL)	>200	0	<12

Table 1. Fractionation Method Comparison for 24 samples.

Automated SPE & GC-FID Approach

The Extrahera™ Classic is an automated SPE extraction system and was utilized to perform EPH fractionation of extracts.

1. Extract samples with hexane.
2. Dry extracts to remove residual water.
3. Set-up Extrahera™ with ISOLUTE® EPH cartridges and samples.
4. Run EPH fractionation method.
5. Aliphatic and aromatic fractions are collected in separate vials.
6. Concentrate using TurboVap® EH at 35°C under N₂ to 1 mL.
7. Analyze via GC-FID.

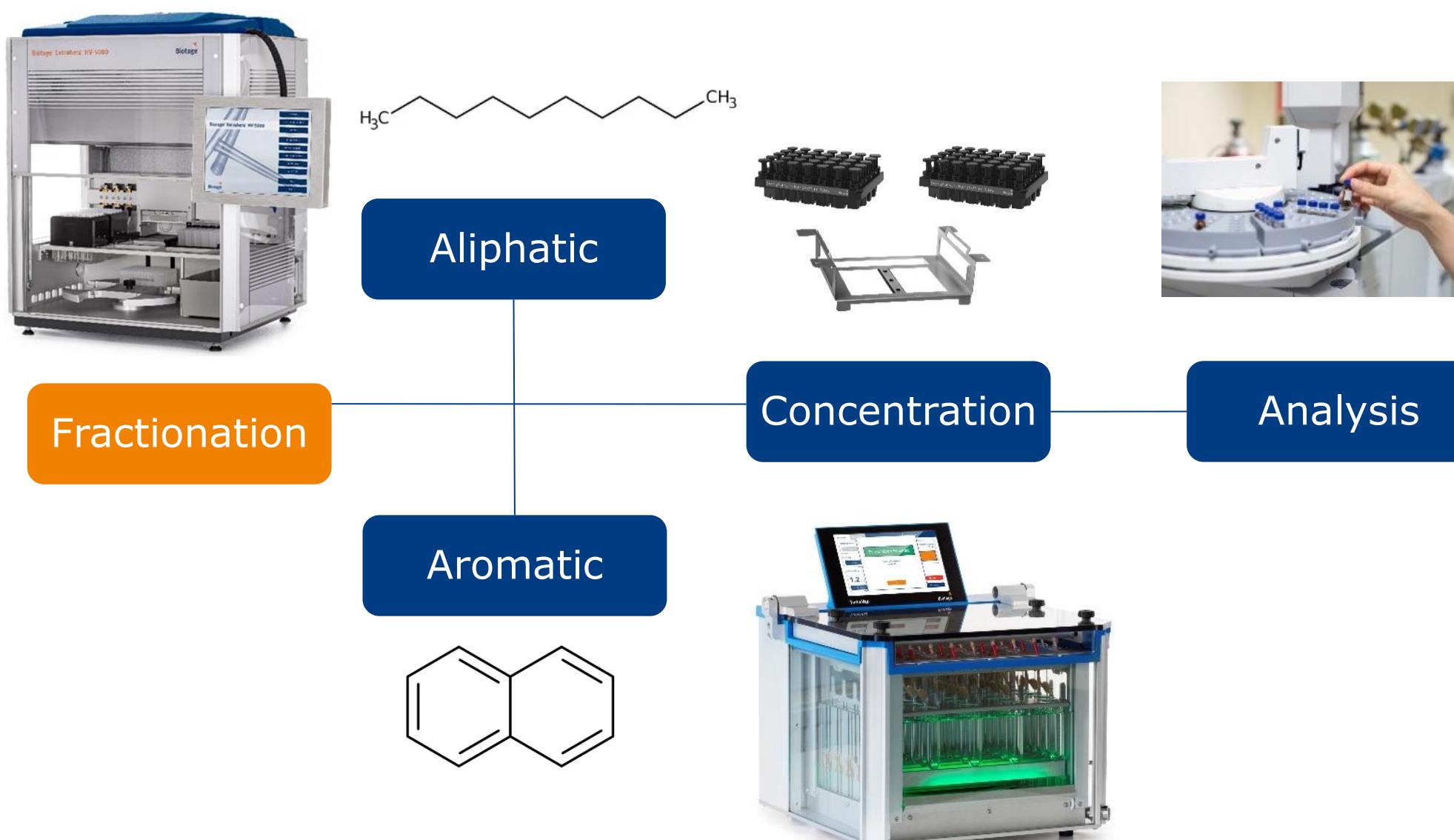


Fig 2. EPH Workflow: Step 2 - Fractionation.

Challenges: Contamination Concerns

The Extrahera™ Classic has some plastic components that caused background contamination within reportable ranges. These mainly came from the sample tips and solvent reservoirs. As the solvents extracted contamination from the plastic components, a visible plastics wave pattern was observed in the chromatograms (particularly within the Aliphatic Range) as shown below in Fig 3.

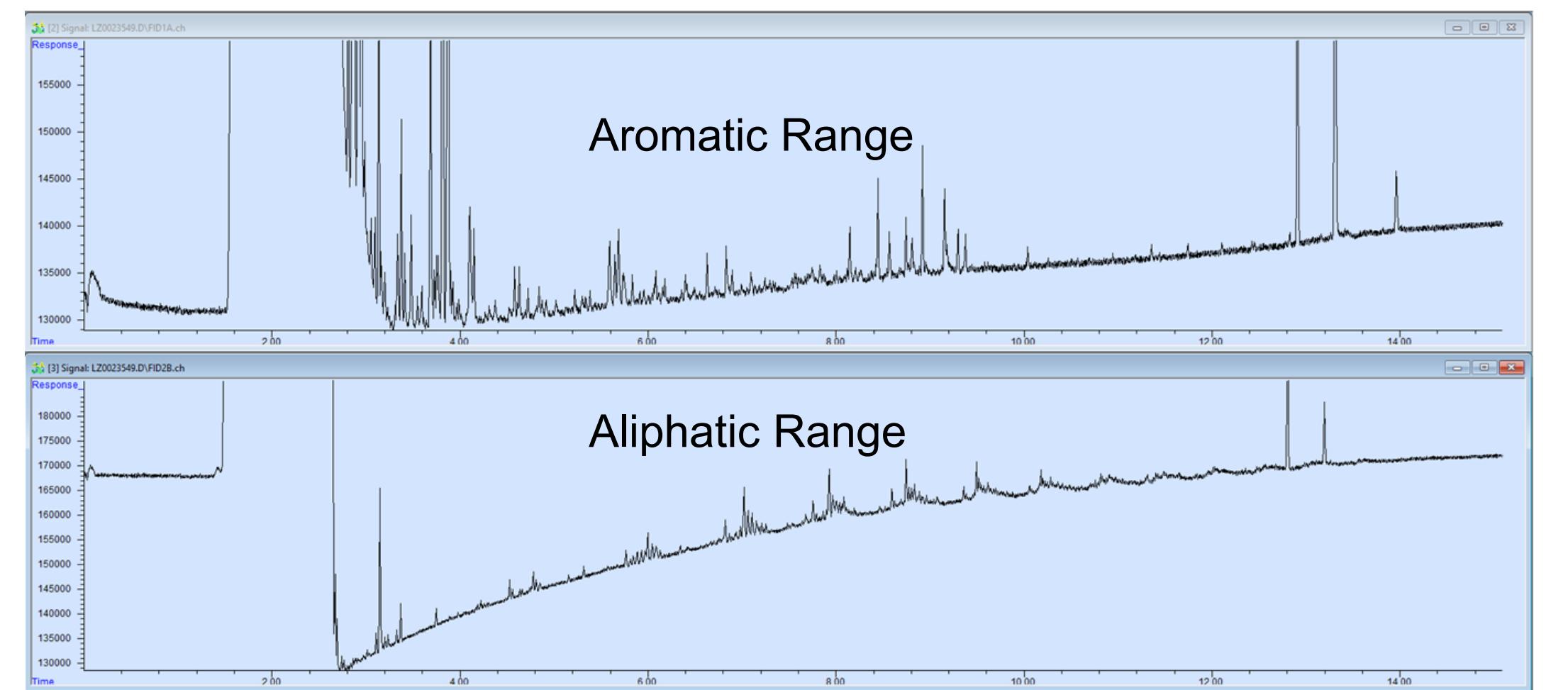


Fig 3. Method Blank Chromatograms: Contamination from Plastic Components

Plastics Detection

Protocols were established to minimize the plastic contamination and produce consistent results for system blank (SB) data. These protocols include but are not limited to MADEP (<5ppm) and RECAP (<1.8ppm). Table 2 shows individual Aliphatic results (in ppm) with the Extrahera™ Classic vs a Fractionator LC System.

Sample ID	Nonane	Decane	Dodecane	Tetradecane	Hexadecane	Octadecane
SPE-SB#1	N.D.	N.D.	0.071	0.061	0.047	0.035
SPE-SB#2	N.D.	N.D.	0.072	0.055	N.D.	N.D.
SPE-SB#3	N.D.	N.D.	0.050	0.047	0.056	0.050
SPE-SB#3	N.D.	N.D.	0.061	0.049	0.040	0.033
FA-SB	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FB-SB	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Table 2. Extrahera™ Classic, Fractionator A, and Fractionator B Aliphatic System Blank Results (ppm). Hexane tip rinse changed from 20 mL/min to 10 mL/min.

Results: Aliphatic Fractionation

Aliphatic recovery was determined by processing laboratory fortified reference matrix spikes with a concentration of 10.0 ppm. Results were compared against HPLC Fractionation and are shown in figure 4 below.

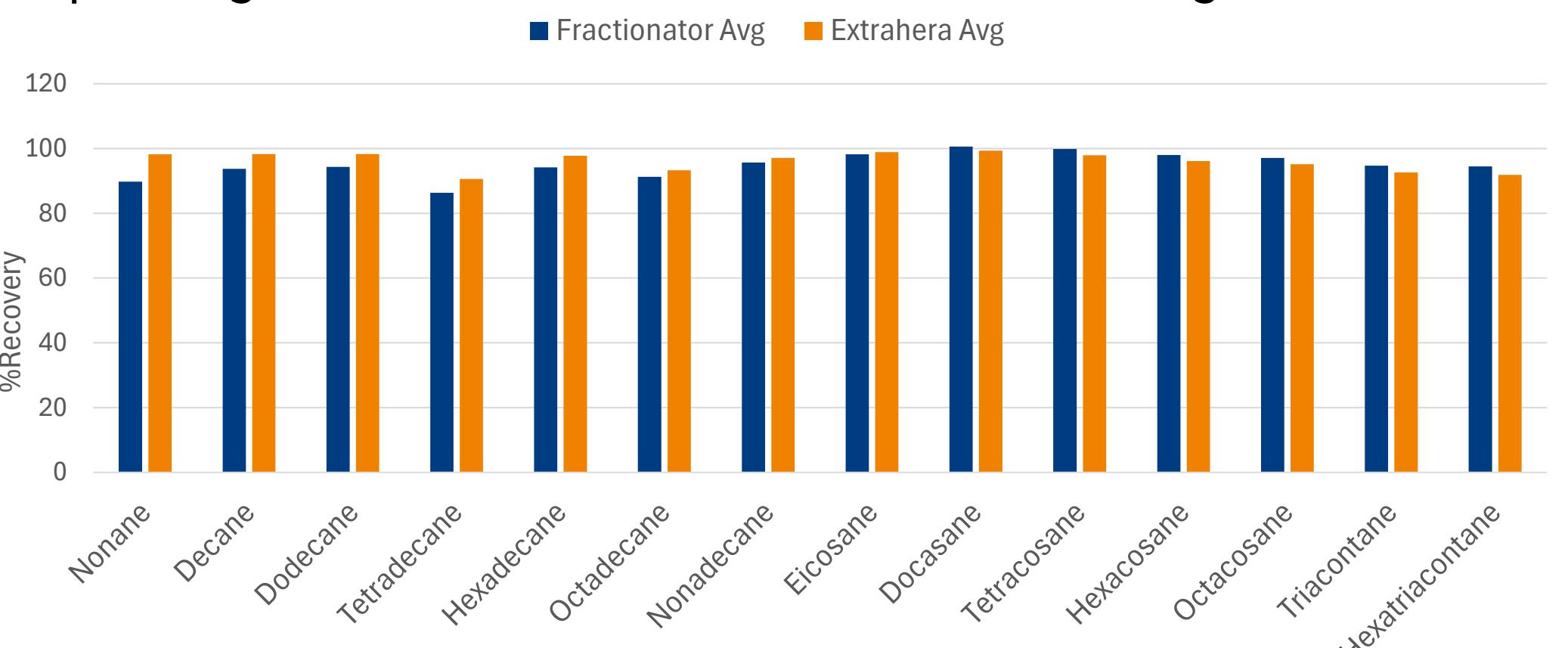


Fig 4. Extrahera™ Aliphatic Recovery

Results: Aromatic Fractionation

Aromatic recovery was determined by processing laboratory fortified reference matrix spikes with a concentration of 10.0 ppm. Results were compared against HPLC Fractionation and are shown in figure 5 below.

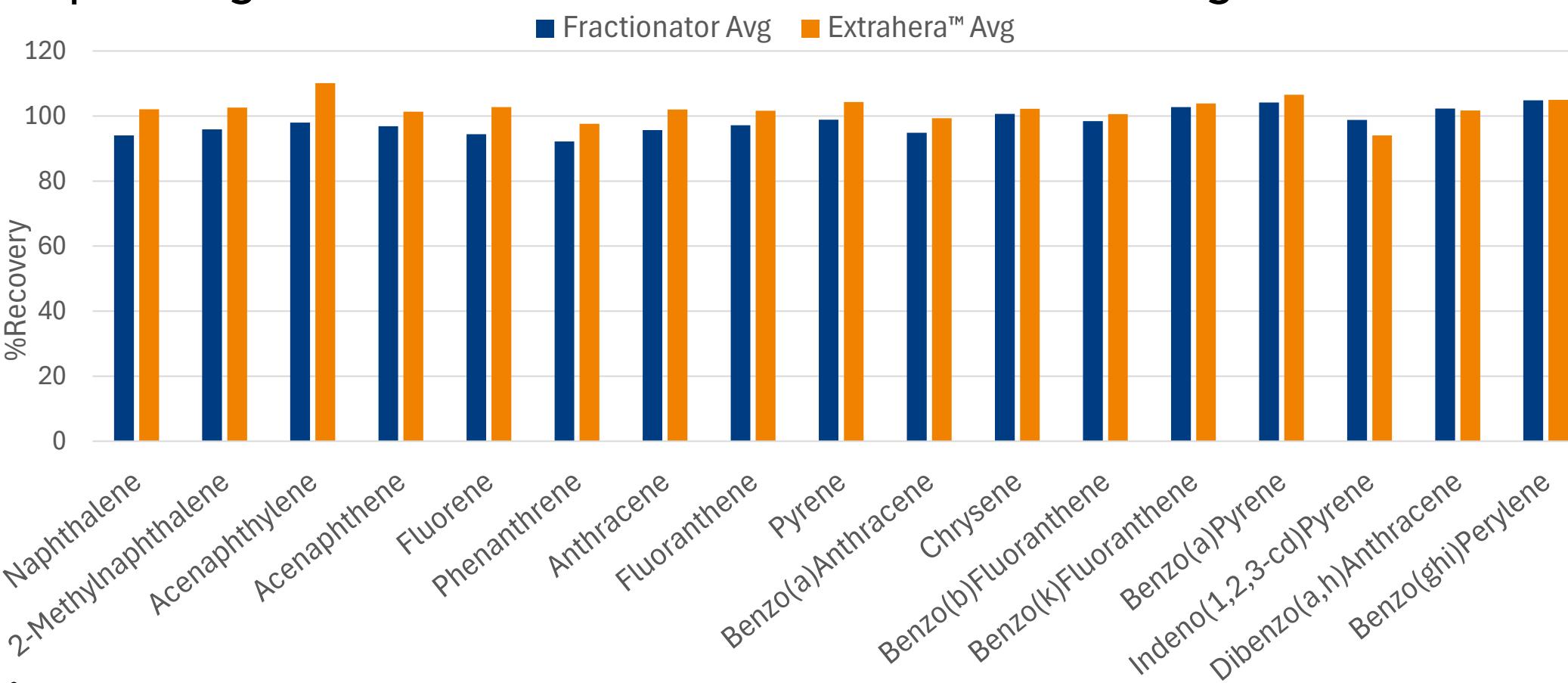


Fig 5. Extrahera™ Aromatic Recovery

Conclusion

The benefits of choosing solid phase extraction over other techniques emphasize solvent reduction, faster processing times, and higher throughput. The findings of this research contribute valuable insights for laboratories seeking to optimize EPH fractionation techniques for more efficient and reliable analyses.

