

Instrument: Paradigm™ GCxGC-FID

A Streamlined Turnkey Solution for Routine Total Petroleum Hydrocarbon Analysis with LECO Paradigm

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Introduction

This application note outlines a GCxGC-FID turnkey solution for the analysis of Total Petroleum Hydrocarbons (TPH) across a potential carbon range of >C8 to C40 using the LECO Paradigm reverse-fill flush flow modulator. This solution was developed within an environmental testing laboratory to ensure robust performance in a high-throughput environment.

Petroleum hydrocarbons comprise a diverse group of compounds that cause widespread and persistent contamination. Their prevalence in soils and groundwater reflects decades of ongoing industrial, commercial, and domestic activities that led to their release into the environment. As petroleum hydrocarbons can distribute and remain through subsurface layers over long periods, they continue to present varied degrees of impact to human health¹ and natural ecosystems. After release into the environment, they can be subjected to various physical, chemical, and biological processes as they migrate through underlying strata and groundwater.

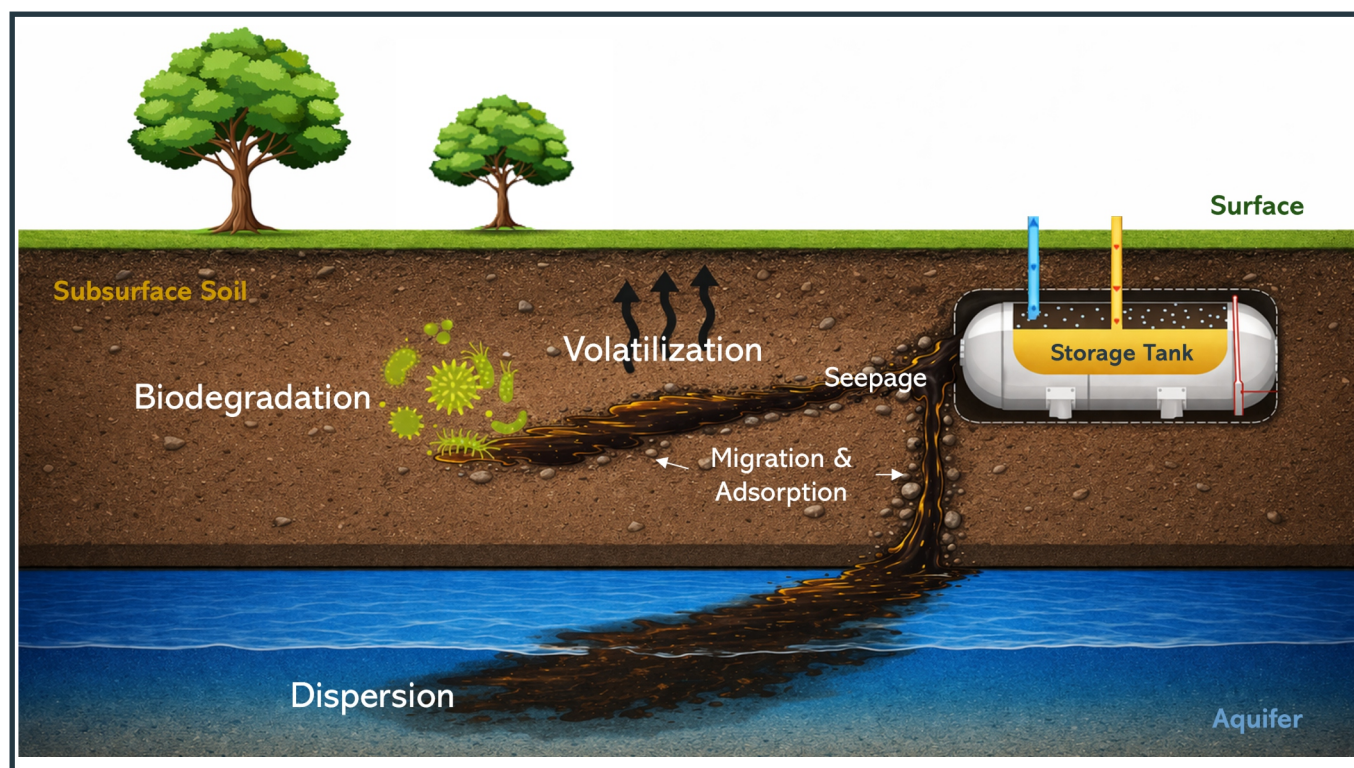


Figure 1. Conceptual schematic of petroleum release from a leaking underground storage tank, illustrating contaminant transport and fate processes in the subsurface, including seepage, migration through soil, adsorption, biodegradation, volatilization, and dispersion within the aquifer. Adapted from CRC CARE (1999)².

In its original unweathered state, petroleum contamination is typically characterized by substantial chemical complexity, potentially comprising hundreds to thousands of individual compounds spanning a wide range of volatilities, polarities, and toxicological properties (Figure 2).¹

This inherent complexity, together with variable physicochemical and biological processes, can generate highly diverse and multifaceted chemical mixtures that present a significant analytical challenge for characterization.

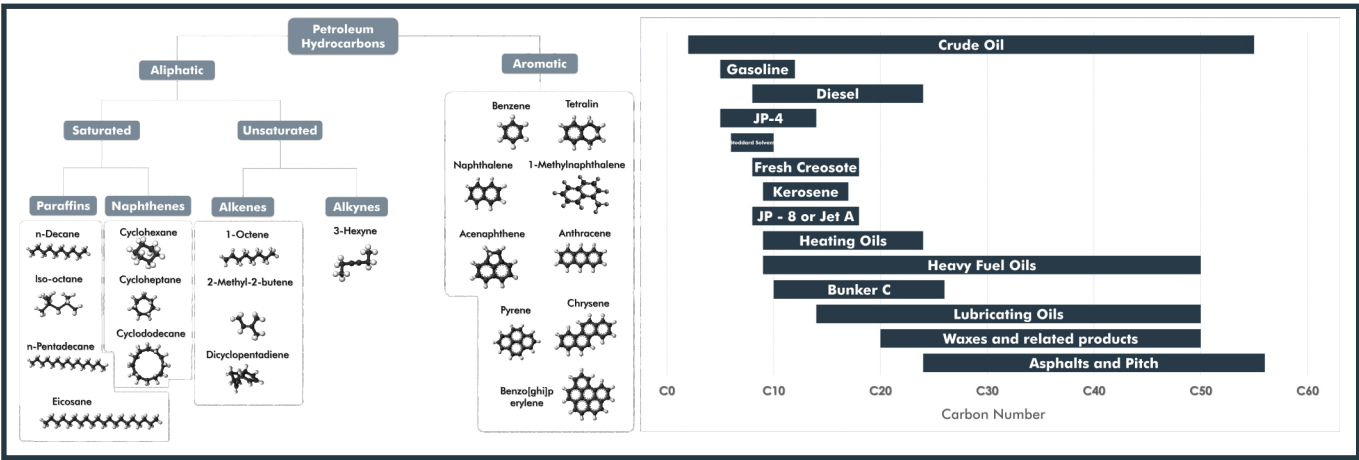


Figure 2. Overview of petroleum hydrocarbon classes showing aliphatic compounds (paraffins, naphthenes, alkenes, and alkynes) and aromatic compounds from monoaromatics to 6-ring PAHs, alongside typical carbon number ranges of petroleum-derived substances spanning light fuels to heavy oils and bituminous materials. Adapted from Harmsen et al.²

To achieve a meaningful framework for risk assessment, contamination can be evaluated by fundamental hydrocarbon classes: aliphatic and aromatic and further grouped into specific carbon ranges prior to quantification. Historically, Solid Phase Extraction (SPE) has been used to fractionate environmental media extracts into aliphatic and aromatic portions, with subsequent analysis of the two aliquots carried out via GC-FID.

LECO Paradigm TPH Workflow Overview

With the Paradigm TPH GCxGC solution, routine analysis of petroleum hydrocarbons is streamlined and simplified within a single-channel GCxGC-FID solution that is engineered for usability and robust, long-term operation. This reflects the evolution of GCxGC into a proven, reliable platform for the modern routine laboratory.³ Table 1 summarizes the GCxGC-FID instrument parameters.

Table 1. Instrument parameters for the GCxGC-FID analysis.

Gas Chromatograph	LECO Paradigm GCxGC-FID
Injection	Pulsed Splitless
Carrier Gas	Hydrogen
Column One	TPH 1st Dimension Column
Column Two	TPH 2nd Dimension Column
2nd Dimension Separation Time	2.6 s, Flush Factor 1.75
Temperature Program	40 °C hold for 1.5 min, ramp 25 °C/min to 350 °C, hold for 2.5 min
FID Data Collection Rate	200 Hz

GCxGC Fractionation: Aliphatic and aromatic separation of a sample extract is achieved during sample acquisition via orthogonal column chemistries (Figure 3). The need for SPE fractionation is therefore eliminated, enabling a single solvent extraction and a single sample injection. This not only streamlines the overall workflow, but also eliminates consumable costs, intensive labor, and variability associated with SPE, reduces waste (i.e., single-use plastic and solvent), and decreases overall solvent volumes used.

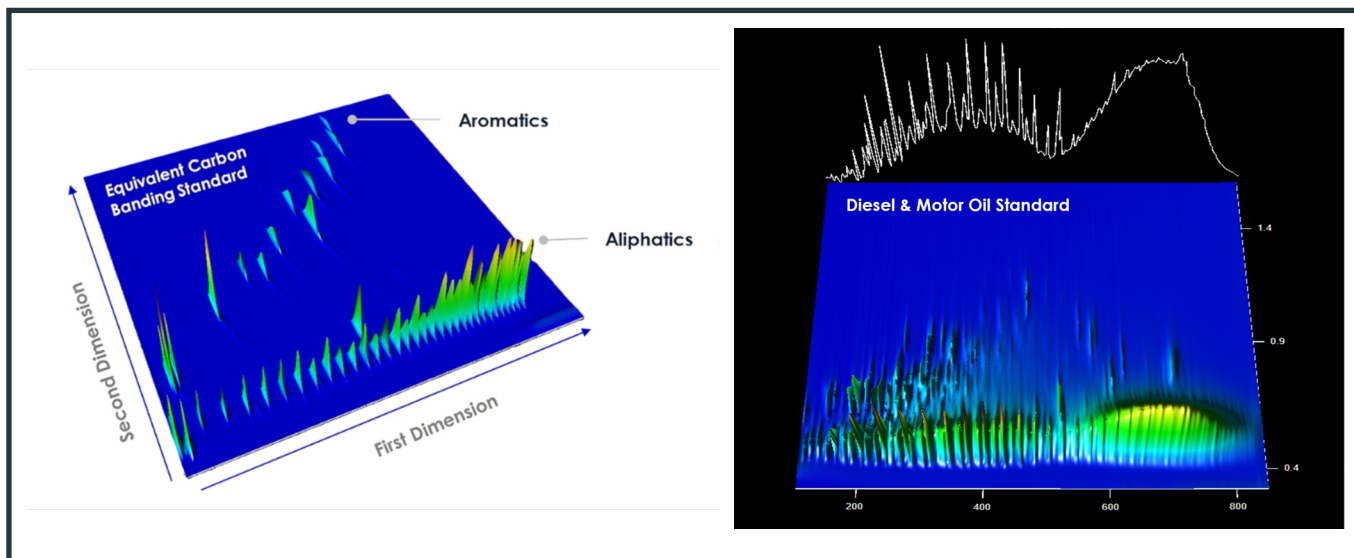


Figure 3. GCxGC 3D surface plot of equivalent carbon banding standard (left), showing the position of the aliphatic and aromatic compounds within the separation space with a corresponding Diesel Range Organics/Oil Range Organics standard (DRO/ORO) and projected 1D trace on the x-axis (right).

Greater Sample Detail: Samples that produce Unresolved Complex Mixtures (UCMs) using one-dimensional GC are resolved and chemically structured, providing greater chemical detail and improving capabilities for contamination source and weathering assessment.

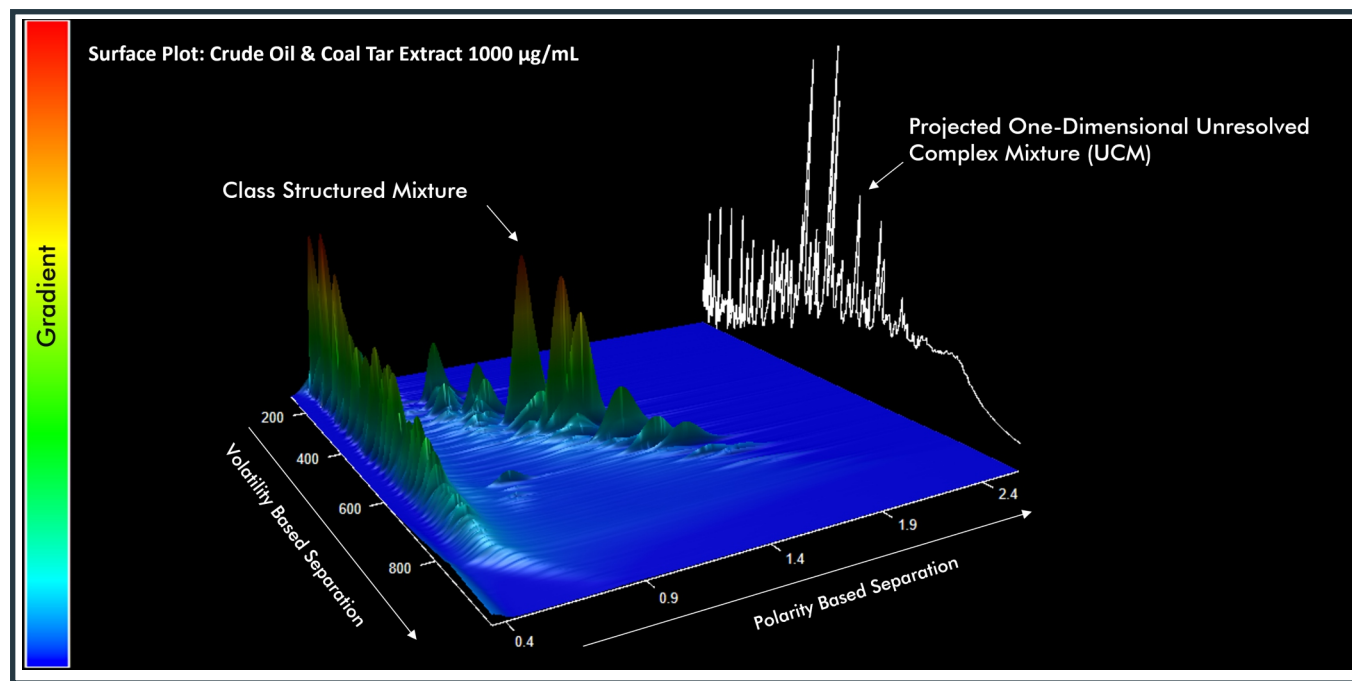


Figure 4. GCxGC 3D surface plot of a crude oil and coal tar extract at 1000 µg/mL, illustrating how class-structured hydrocarbon composition becomes resolved in two-dimensional separation space, while the corresponding projected one-dimensional trace appears as an unresolved complex mixture (UCM).

Classifications and Reporting: With aliphatic and aromatic content completely separated, equivalent carbon regions are defined with a simple classification procedure using the retention times of an n-alkane series. This classification template with defined regions is then automatically applied with peak integration to all calibration standards, quality controls, and automatically exported and imported to a dedicated spreadsheet for quantitation and reporting (see Figure 5).

Globally, carbon band groupings can vary significantly by region and by report type⁴. By using a universal standard that groups carbon bands into individual equivalent carbon classification regions, i.e. >C8 – C9, >C9 – C10 etc., multiple report types can be generated from a single file export (i.e., TPH CWG, Total TPH, WAC etc.).

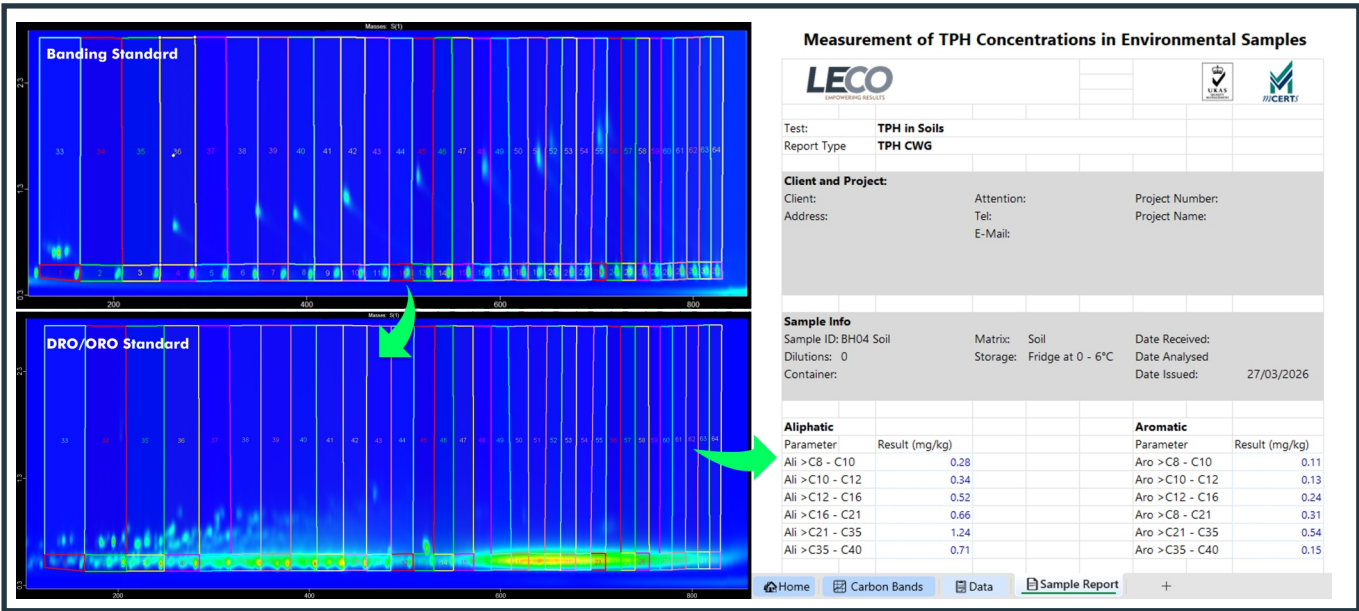


Figure 5. A universal classification template defined from an equivalent carbon banding standard covering aliphatic and aromatic regions from >C8 to C40, subsequently applied to a Diesel Range Organics/Oil Range Organics (DRO/ORO) standard with a succeeding TPH CWG (Criteria Working Group) style report of a sample in which the required banding concentrations were derived from the universal classification regions.

Processing Speed: Data processing speed is an important consideration, especially in high-throughput environments where faster turnarounds are required. Rapid data processing greatly increases productivity when large numbers of files are collected each day or if samples need re-analysis. To ensure no bottlenecks exist in the workflow, the average processing time for this solution is ~5 seconds per sample. Retrospective alterations to individual sample files can also be carried out quickly.

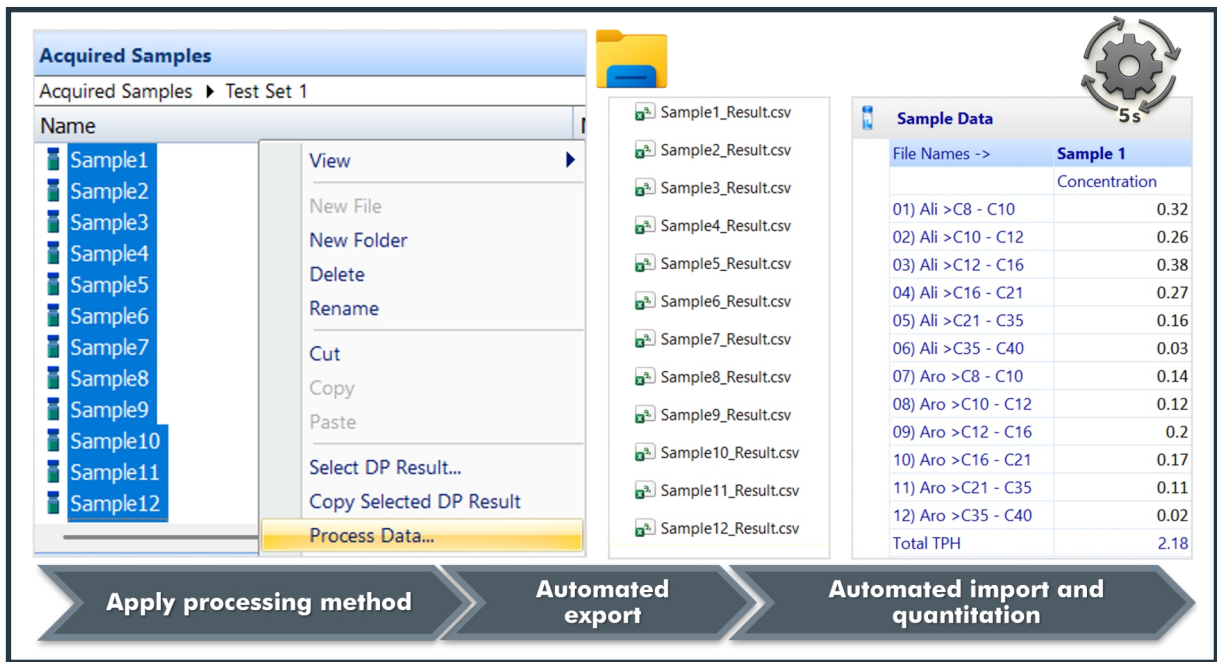


Figure 6. Automated data processing, export, and quantitation completed in ~5 seconds per sample.

Automated Flow Balancing: Accurate modulator flow balancing is essential for reliable quantitation. With LECO's *Paradigm* reverse fill-flush modulator, this process is a fully automated and precise operation within the *ChromaTOF* software. Assurance of accuracy is achieved with a simple, automated check. For this procedure, n-alkanes from n-C8 to n-C30 are injected in GCxGC and GC modes within a single acquisition sequence with no hardware change. The results of a balancing check procedure are shown in Figure 7, with Relative Difference Percentages (RDP) comparisons of the GC and GCxGC peak areas confirming full analyte transfer was achieved during modulation and injection of analytes to the secondary column.

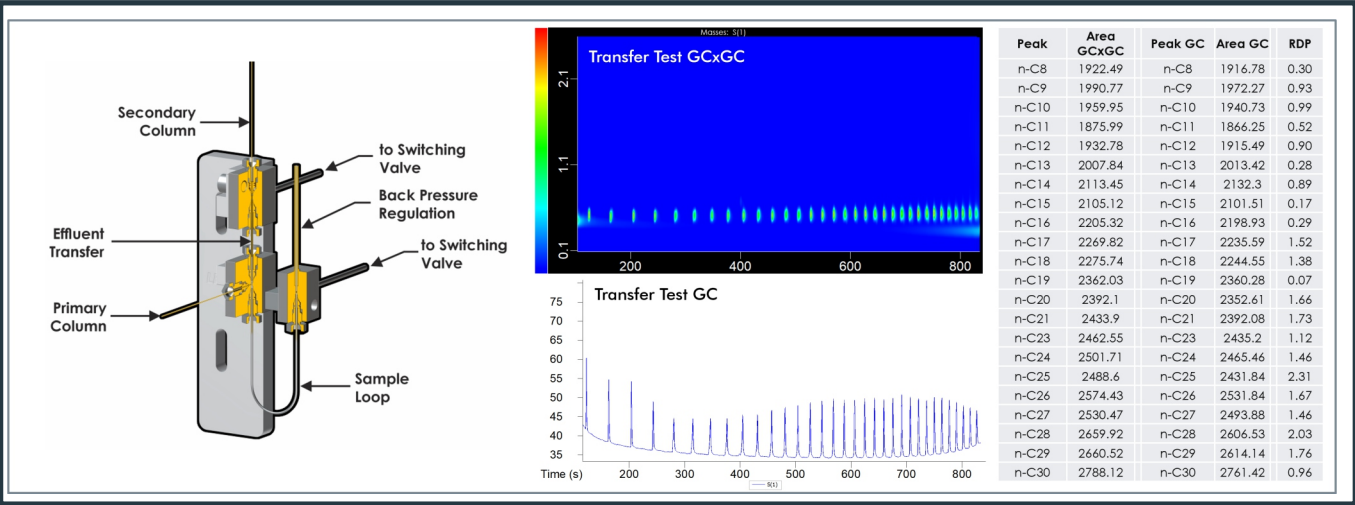


Figure 7. Schematic of the *Paradigm* reverse fill-flush modulator (RFF) and results of the automated flow balancing procedure with the acquired GCxGC and GC peaks from nC8 to nC30 and their Relative Difference Percentages (RDP).

Practical Modulator Handling: Modulator accessibility is essential for reliable and efficient operation. The *Paradigm* primary and secondary column ports are adequately spaced to allow convenient access, facilitating accurate leak checking whilst significantly reducing the risks of column breakage and plate blockage. Column swaging is simple and straightforward with pre-set insertion depths.

Interchangeable Guard Column: To achieve a more robust operation when running sample extracts of dirty matrices such as soils and sludges, a short guard column is utilized. This extends the potential lifespan of the primary column and maintains stable 1D and 2D retention times after inlet maintenance by eliminating the need to trim the primary column when contamination occurs. The primary column remains connected each time the guard column is swapped, reducing leak introduction potential, and the union uses the same flexi-metal ferrules as the *Paradigm* modulator.

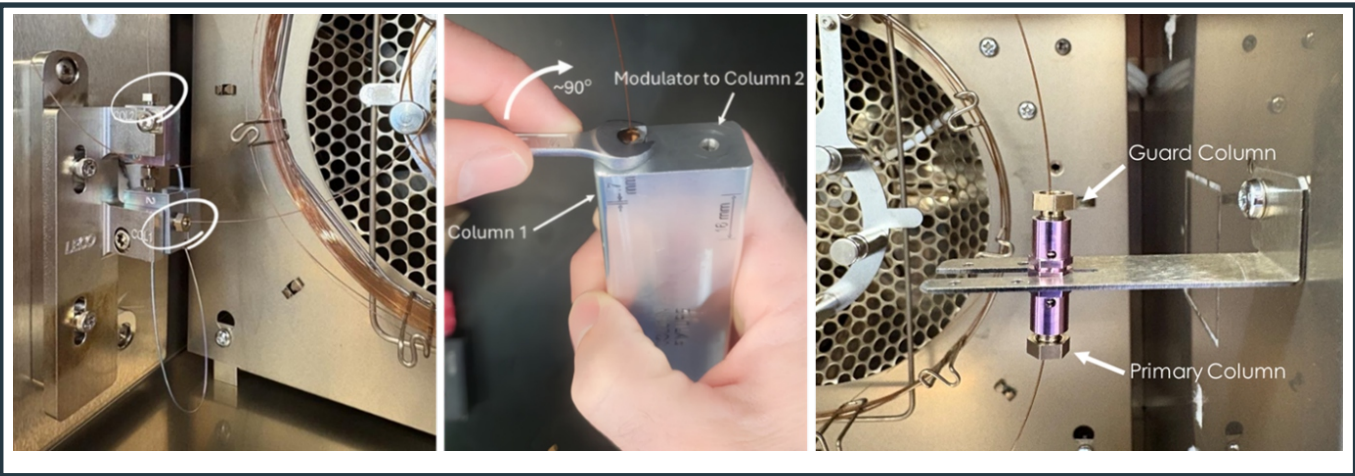


Figure 8. Location of *Paradigm* ports for the primary and secondary GCxGC column. Illustration of the simple swaging process. The guard column and primary column position in the union.

Workflow Summary: TPH with *Paradigm* is a streamlined, high-throughput solution that simplifies petroleum hydrocarbon analysis while improving sample resolution and operational robustness.

- Aliphatic and aromatic separation occurs during acquisition, eliminating the need for SPE fractionation, and enabling a single sample extract and a single injection.
- SPE waste is eliminated, reducing sample preparation complexity, solvent use, consumable cost, and plastic waste.
- Enhanced chromatographic resolution reveals greater chemical detail for improved data interpretation.
- Simple carbon-band-based classification supports fast, consistent data processing with flexibility in reporting types generated.
- Automated modulator flow balancing within *ChromaTOF* supports reliable quantitation.
- Robust modulator design enables stable long-term operation with minimal downtime.

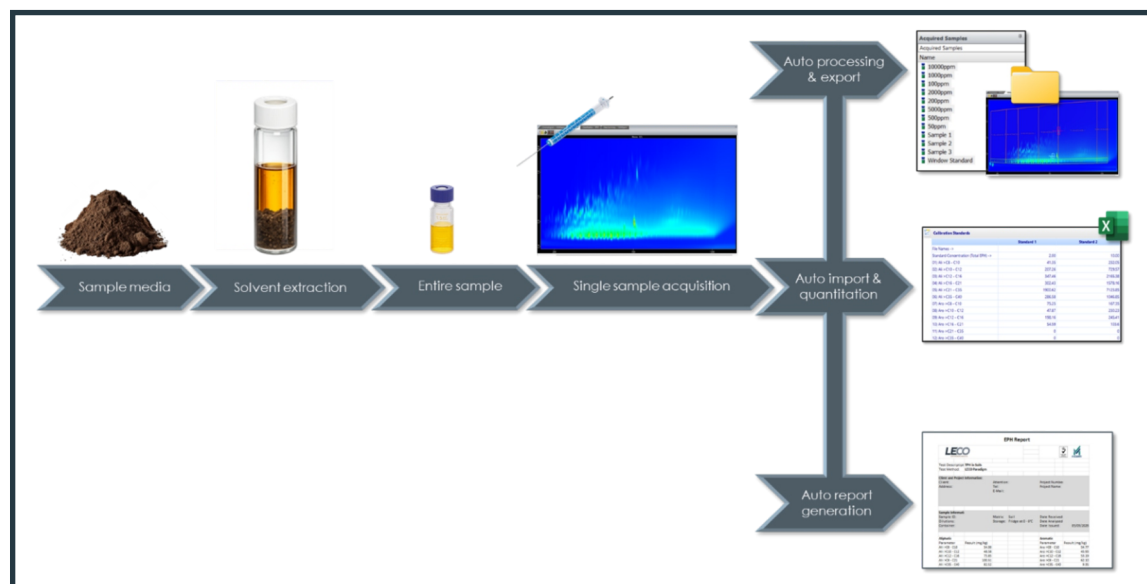


Figure 9. GCxGC-FID workflow for TPH analysis using the LECO Paradigm system. The entire extract is injected once. Aliphatic and aromatic separation occurs during single-sample acquisition, enabling automated carbon band quantitation, data export, and report generation within a streamlined workflow.

Results and Discussion

Linearity and Detection Limits: The solution is calibrated across a wide dynamic range to allow quantitation of trace-level contamination and heavily impacted matrices. Low detection limits are achieved with a calibration range from 2 µg/mL to 5000 µg/mL (total EPH) to facilitate broad quantitation across matrices such as soils, water, and sludges.

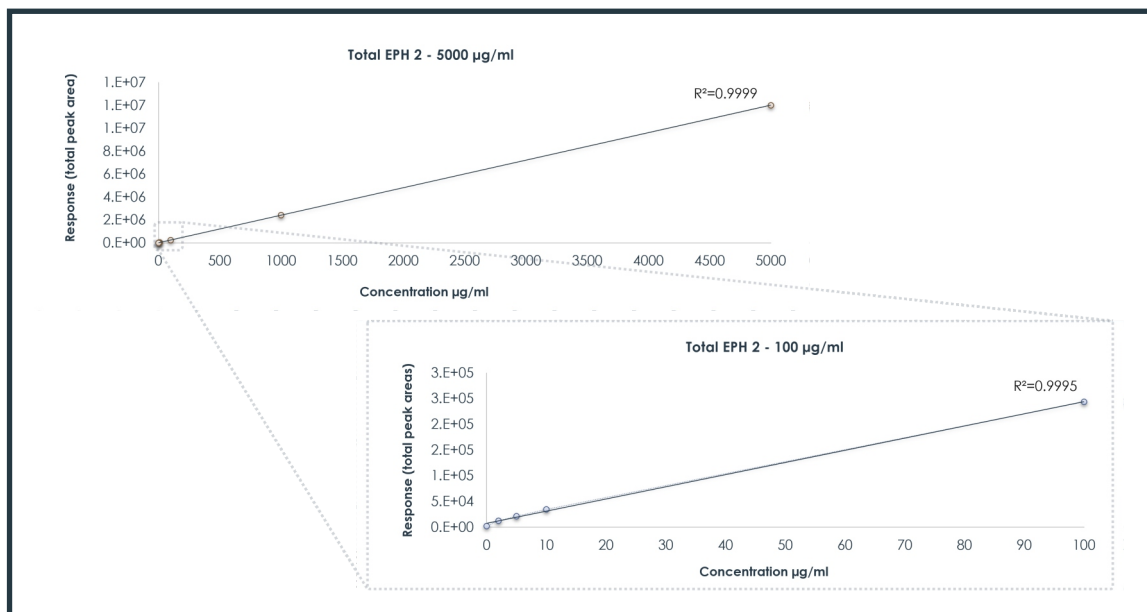


Figure 10. Calibration range for total TPH. Note: If a higher calibration range is required, this is achievable, e.g., 50 µg/mL to 20,000 µg/mL.

Repeatability: To ensure reliable system performance during routine operation, 10 injections of a mid-range standard (1000 $\mu\text{g/mL}$) and low-level standard (5 $\mu\text{g/mL}$) were injected across a sequence of 80 soil and water sample extracts. This was immediately followed by 15 injections of a surrogate standard containing 2-Fluorobiphenyl and p-Terphenyl at individual concentrations of 1 $\mu\text{g/mL}$. Excellent precision was achieved throughout.

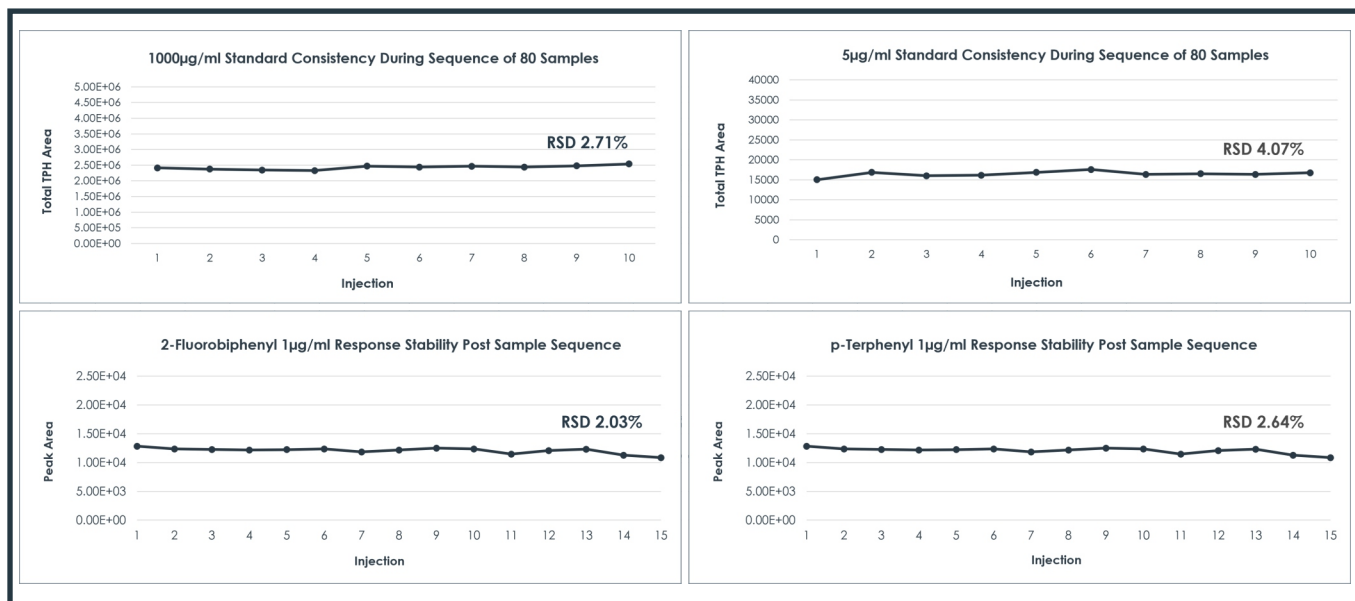


Figure 11. Analytical stability during extended sequence operation. Ten injections of mid-range (1000 $\mu\text{g/mL}$) and low-level (5 $\mu\text{g/mL}$) TPH standards were analyzed across 80 soil and water sample extracts, followed by 15 injections of surrogate standards (2-Fluorobiphenyl and p-Terphenyl, 1 $\mu\text{g/mL}$ each). Consistent responses demonstrate excellent precision throughout the sequence.

Carryover Assessment: To assess the potential for carryover, a 10% (100,000 $\mu\text{g/mL}$) crude oil diluted in n-hexane was introduced into the system. It was immediately followed by an n-hexane blank injection in pulsed splitless mode. The blank contained no detectable peaks, providing assurance of system cleanliness and zero carryover when analyzing samples. See Figure 12.

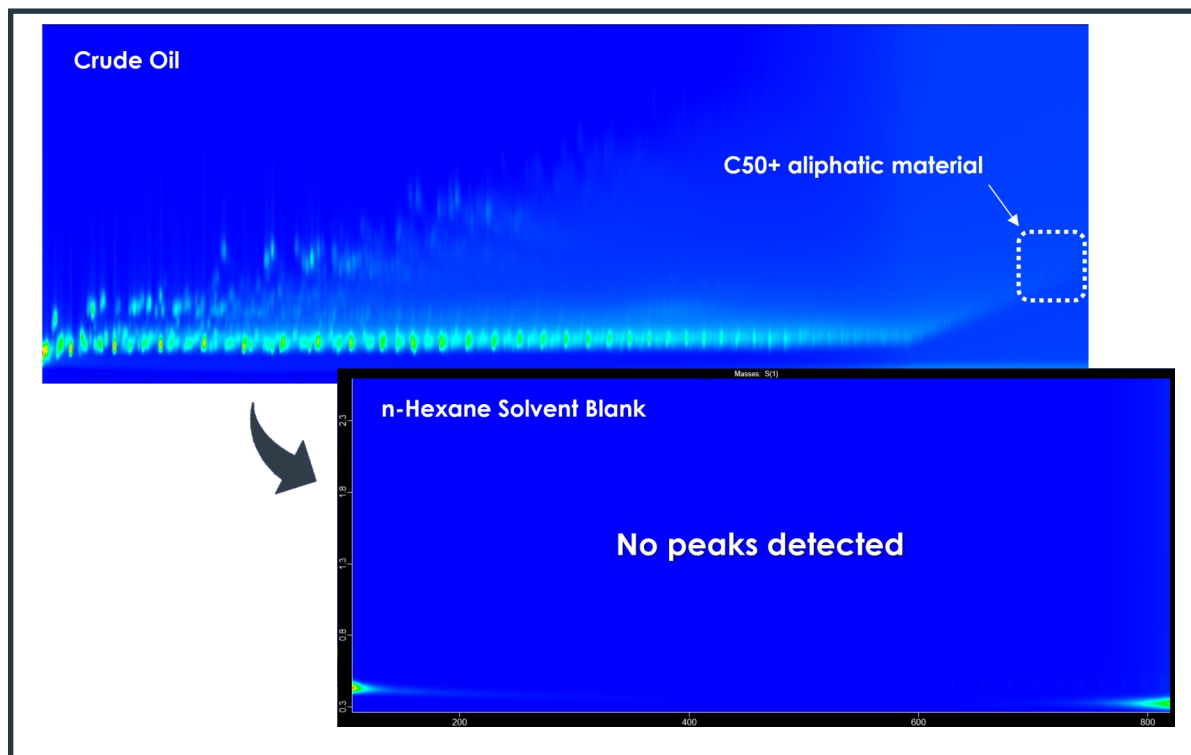


Figure 12. GCxGC contour plot of 10% crude oil showing resolved aliphatic hydrocarbons extending beyond C50, followed by a solvent blank confirming negligible carryover and effective system cleanliness.

High-Molecular-Weight Aromatics and Wraparound: Sample extracts containing source contamination from media such as coal tar can introduce higher ring-number polycyclic aromatic hydrocarbons. Available 2D separation space is necessary to avoid such compounds wrapping around and affecting quantitation results. The method maintains adequate 2D space to ensure PAHs containing six or more fused aromatic rings are captured within the correct modulation.

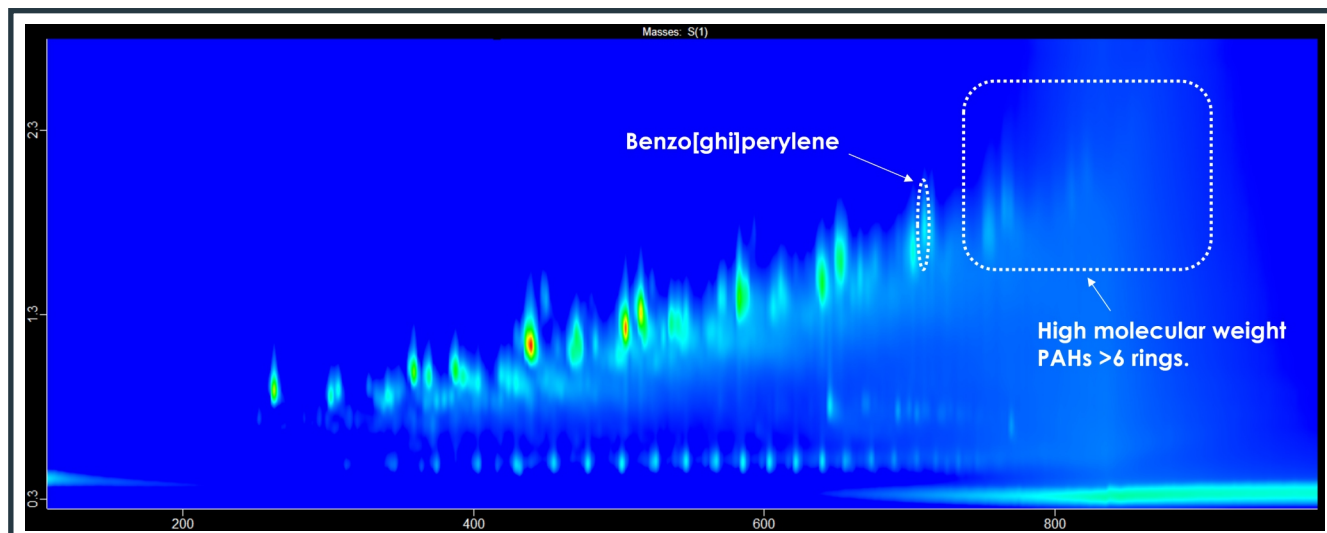


Figure 13. GCxGC contour plot of a coal tar extract highlighting the position of benzo[ghi]perylene and high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) containing greater than six fused aromatic rings.

Non-Petroleum Compounds: With any TPH GCxGC method that eliminates SPE, non-petroleum hydrocarbons and biogenic substances may be extracted and injected into the system. With the *Paradigm* TPH solution, it's possible to map and isolate such substances and readily exclude them from quantitation results.

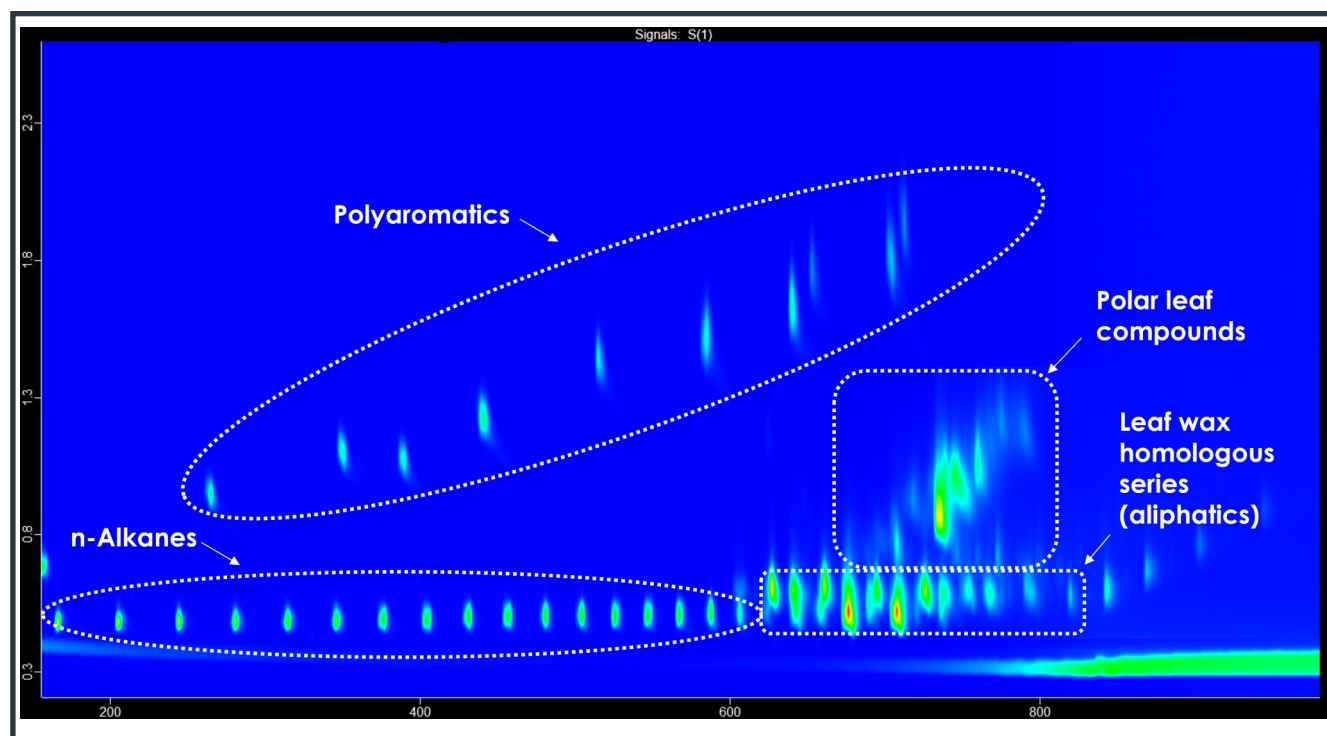


Figure 14. Leaf mulch extract combined with an equivalent carbon banding standard containing n-alkanes and polycyclic aromatic hydrocarbons (PAHs). The polar plant wax compounds include fatty alcohols and fatty acids. Note: the aliphatic content derived from the extracted leaf would elute within the aliphatic portion of an SPE fractionation.

Conclusion

This application note has outlined a streamlined workflow for the routine analysis of total petroleum hydrocarbons from >C8–C40 in environmental media using the robust and user-friendly LECO *Paradigm* reverse-fill flush flow modulator. The need for Solid Phase Extraction (SPE) is eliminated, significantly reducing the cost, labor, solvent consumption, and plastic waste of sample preparation. A simple, flexible, and automated processing workflow facilitated by *ChromaTOF* software enables rapid data reporting. The solution achieves low detection limits, a wide dynamic range, and demonstrates excellent repeatability across extended sample sequences with no detected carryover. High-molecular-weight PAHs are captured and biogenic substances are separated enabling their removal from quantitation results. Overall, the *Paradigm* GCxGC turnkey TPH solution provides a robust, high-throughput, and simplified solution for the routine analysis of TPH.

References

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- ^[2] McLaughlan, RG, Merrick, NP & Davis, GB 2006, Natural attenuation: a scoping review, CRCCARE Technical Report no.3, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia
- ^[3] Misselwitz, M. Research Hype to Practical Analysis: Benefits of Comprehensive Two-Dimensional Gas Chromatography (GCxGC) for a Routine Laboratory.
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