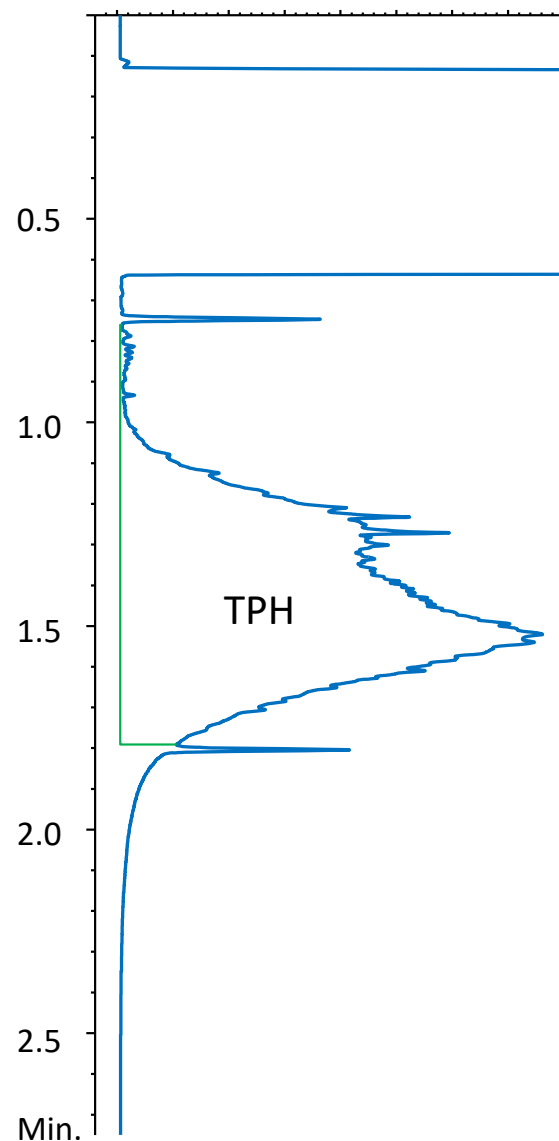# Ultra-fast Gas Chromatography Analysis of Total Petroleum Hydrocarbon Contamination in Soil and Sediment Using Unique Direct Column Heating

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DE44396.5563194444

Total Petroleum Hydrocarbon Analysis (TPH) with ISO 16703

Method Scope
- C_{10} to C_{40} hydrocarbon contamination in the environment
- Accumulation of middles distillates (i.e. diesel) and lubricating oils
- Water, soil, and sediments
- 100 mg/kg to 10,000 mg/kg
- Measure TOTAL hydrocarbons, speciation not needed

- Sample Analysis
- Complex sample preparation to extract hydrocarbons from matrix
- GC analysis of extracts with FID
  - Methods similar to simulated distillation (SimDis)
  - High temperature GC (40 ^{o}C to 350 ^{o}C programming)
  - Need to precisely identify C_{10} and C_{40} RT markers
  - Low B.P. discrimination a key requirement to achieve accurate quantification

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TPH Using Ultra-Fast Gas Chromatography (UFGC)
No compound speciation makes TPH ideally suited to UFGC
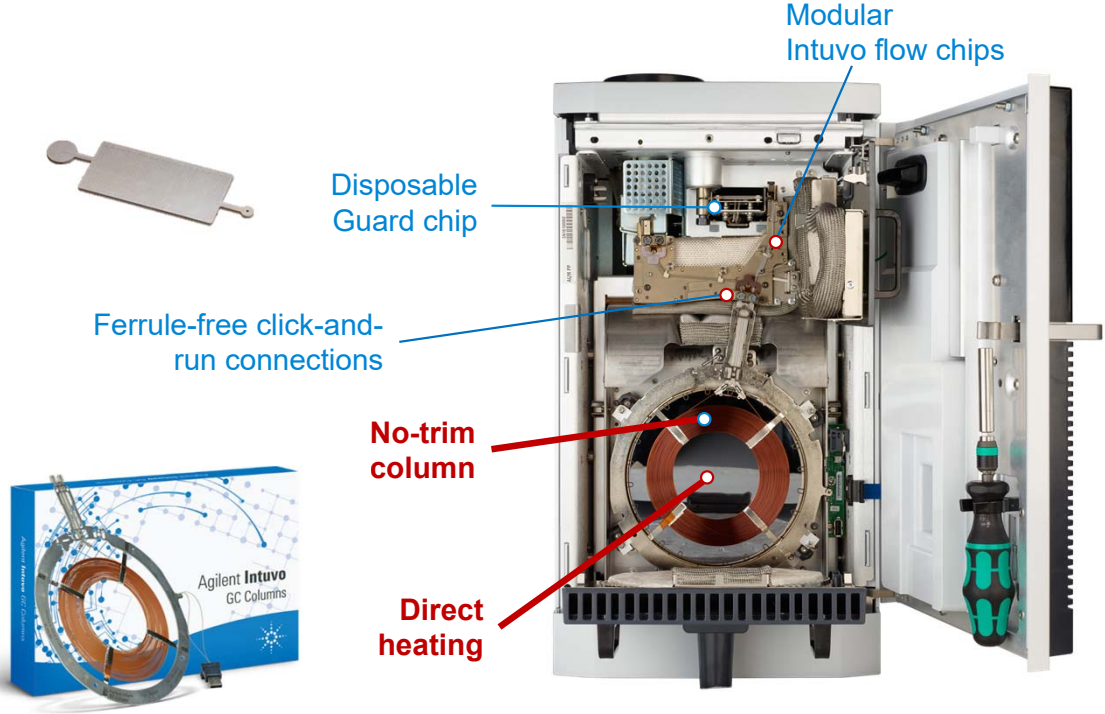
- UFGC Analysis typically 1-3 minutes
  - Rapid column heating (> 100 ^{o}C/min over entire oven temp range)
  - Short columns (3 - 5 m)
  - High carrier flow rates (> 5 mL/min)

- UFGC Challenges
  - Retention Time Precision
    - precise column temperature control
    - precise flow control during fast column heating
  - Column lifetime
    - rapid column heating to high temperatures (350 ^{o}C) degrades:
      - direct column heating elements
      - polyimide coating
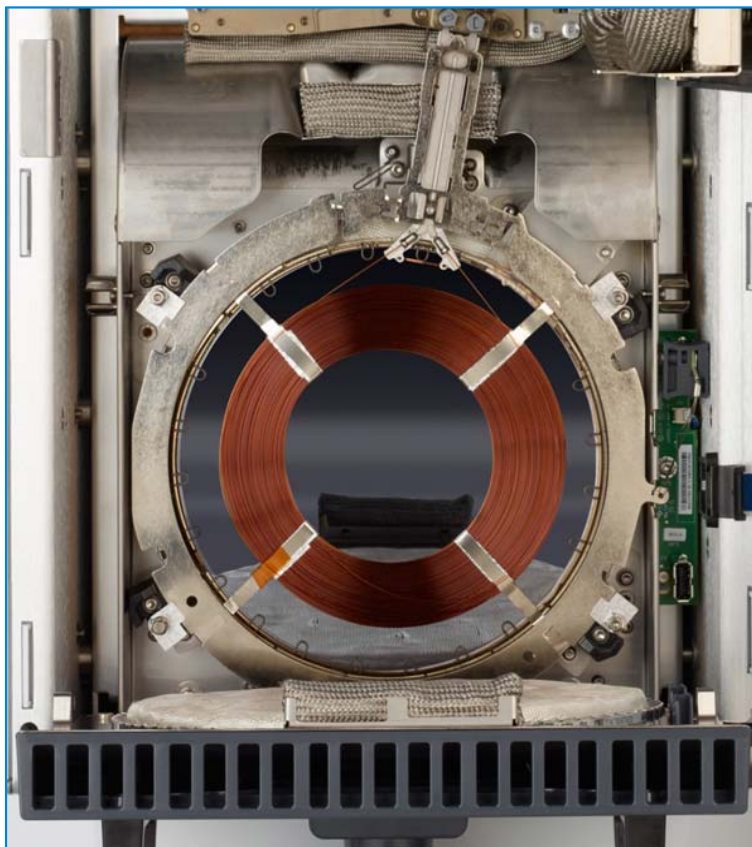   - stationary phase

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A New Approach to Ultra-Fast GC

- Easier

- **Faster**

- Smaller

- Smarter

- Greener

A New Approach to Ultra-Fast GC

Modular
Intuvo flow chips

Disposable
Guard chip

Ferrule-free click-and-
run connections

**No-trim
column**

Agilent **Intuvo**
GC Columns

**Direct
heating**

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Fast Direct Heating and Cooling

- Fast, efficient heating

- Ballistic cooling

- Smaller footprint

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GC Designed for UFGC

- New Column Heating Technology
  - Unique approach to direct column heating
  - 250 ^{o}C/ min over entire oven programming range (40 ^{o}C to 450 ^{o}C)
  - Fewer column elements to fail
    - no complex direct heating/sensing elements
    - no complex in-oven connections

- Next Gen EPC
  - Works with New Column Oven to delivers precise carrier flow during rapid column heating
  - assures retention time and detector response stability

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GC Conditions for UFGC TPH Analysis

Certified Reference Standards purchased from Bundesanstalt für Materialforschung und –prüfung (BAM)

- Soil and river sediment sample matrices
- Real samples with certified consensus TPH values
- Samples prepared at Agilent using ISO 16703 protocol
  - Ultrasonic liquid/solid extraction, centrifuge fines, liquid/liquid cleanup, SPE final cleanup

Intuvo GC Conditions:

- Injection size: 0.5 μL
- S/SL Inlet: splitless mode, Focus liner (p/n 210-4022-5), 350 ^{o}C
- Guard Chip temperature: Track Oven Mode
- Bus temperature: 350 ^{o}C
- DB-1ht column, **5 m x 0.32 mm ID x 0.1 μm**
  - helium carrier gas @ **10 mL/min constant flow**
  - oven program, 40 ^{o}C for 0.5 min, **250 ^{o}C/min** to 350 ^{o}C, hold 0.5 min
- FID: 350 ^{o}C

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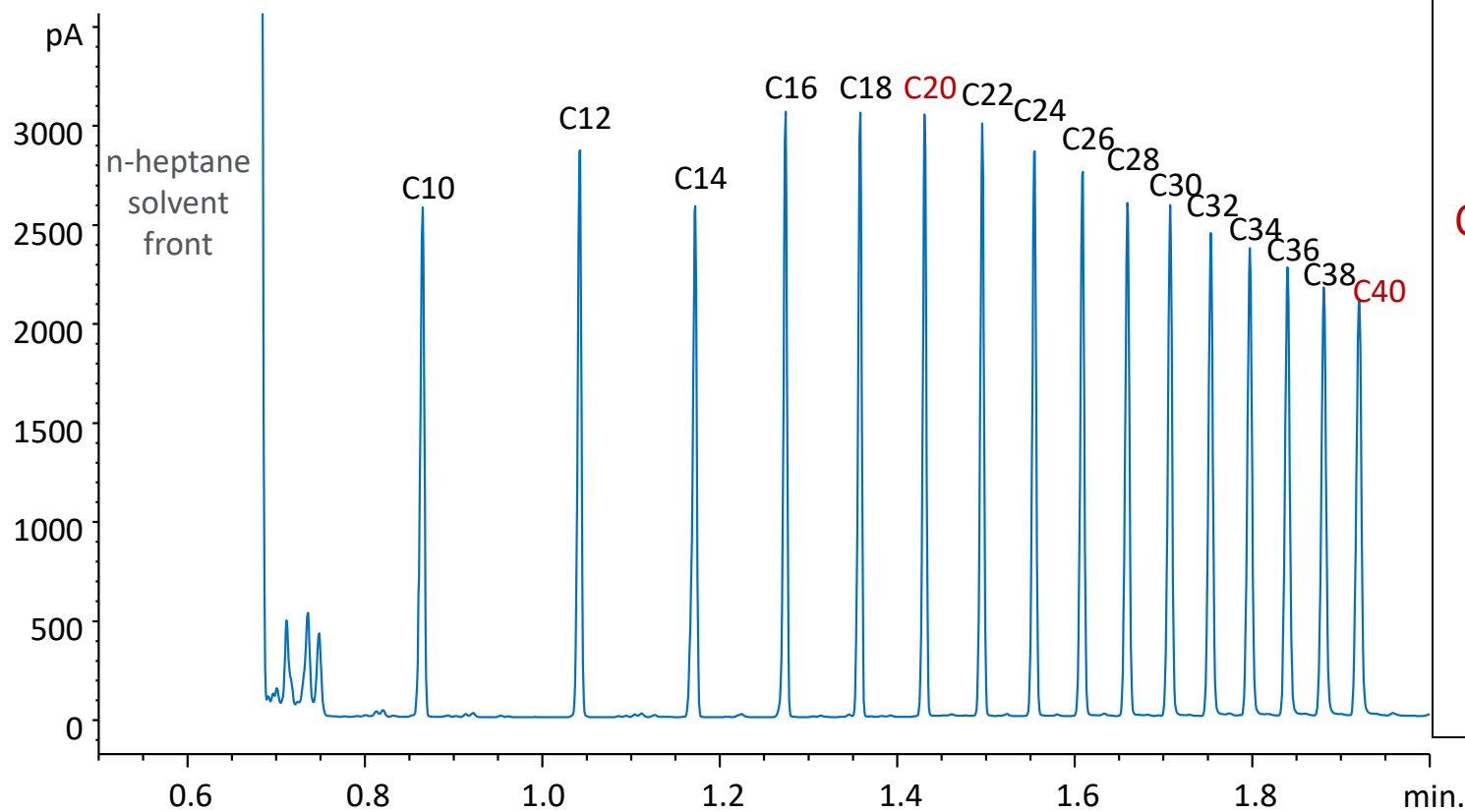# Long-term Chromatographic Stability UFGC TPH Performance Standard

Injection #1
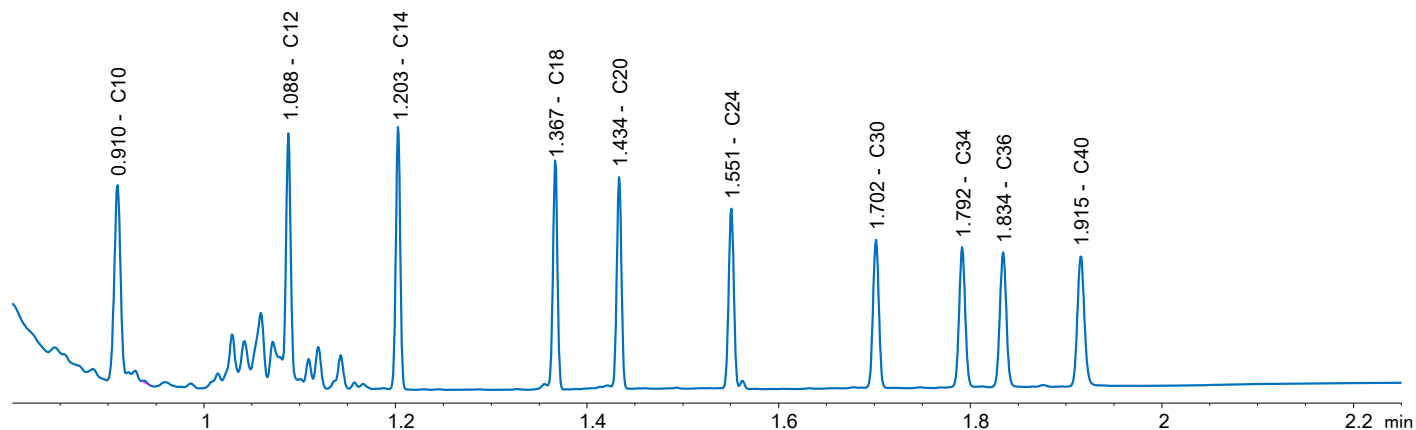
Injection #1500
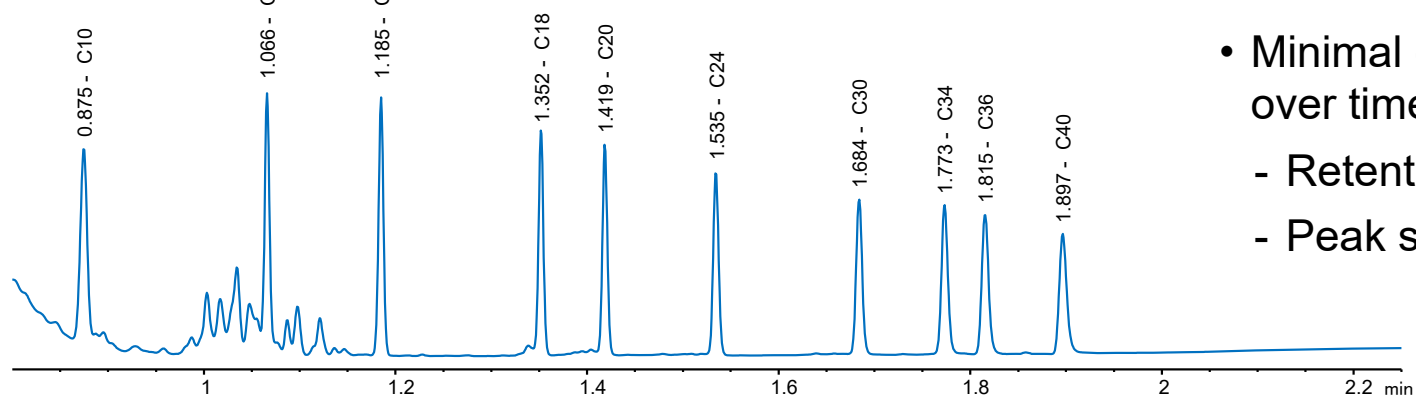
- Minimal change in chromatography over time
 - Retention time
  - Peak shape

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UFGC TPH Discrimination Performance Test
ISO 16703: C40 recovery must be > 0.80

	Peak Area	Recovery
C10	861	0.98
C12	867	0.98
C14	877	0.99
C16	890	1.01
C18	875	0.99
C20*	882	1.00
C22	882	1.00
C24	882	1.00
C26	873	0.99
C28	846	0.96
C30	867	0.98
C32	859	0.97
C34	853	0.97
C36	853	0.97
C38	829	0.94
C40	817	0.93

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UFGC TPH Repeatability Test – 3 Runs of Mid-Level Calibration Standard
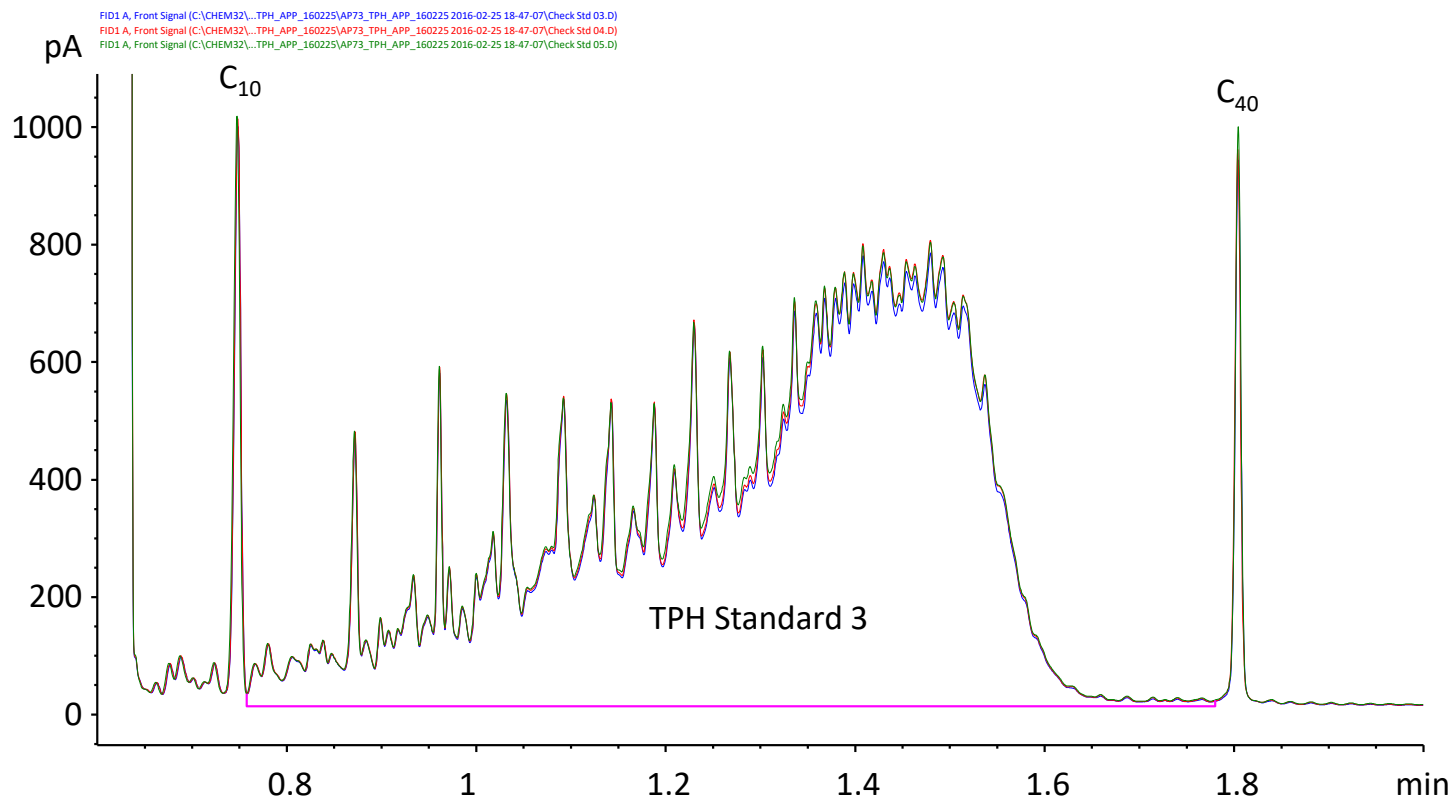
Run	Std 3 Peak Area
1	17644
2	18044
3	18236
Mean	17975
Std Dev	301.9
RSD	**1.7%**

ISO 16704 RSD <= 5%

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TPH Calibration for UFGC Application

Peak Area = 17005.7346 * Amt + 52.100781

Correlation: 0.99983

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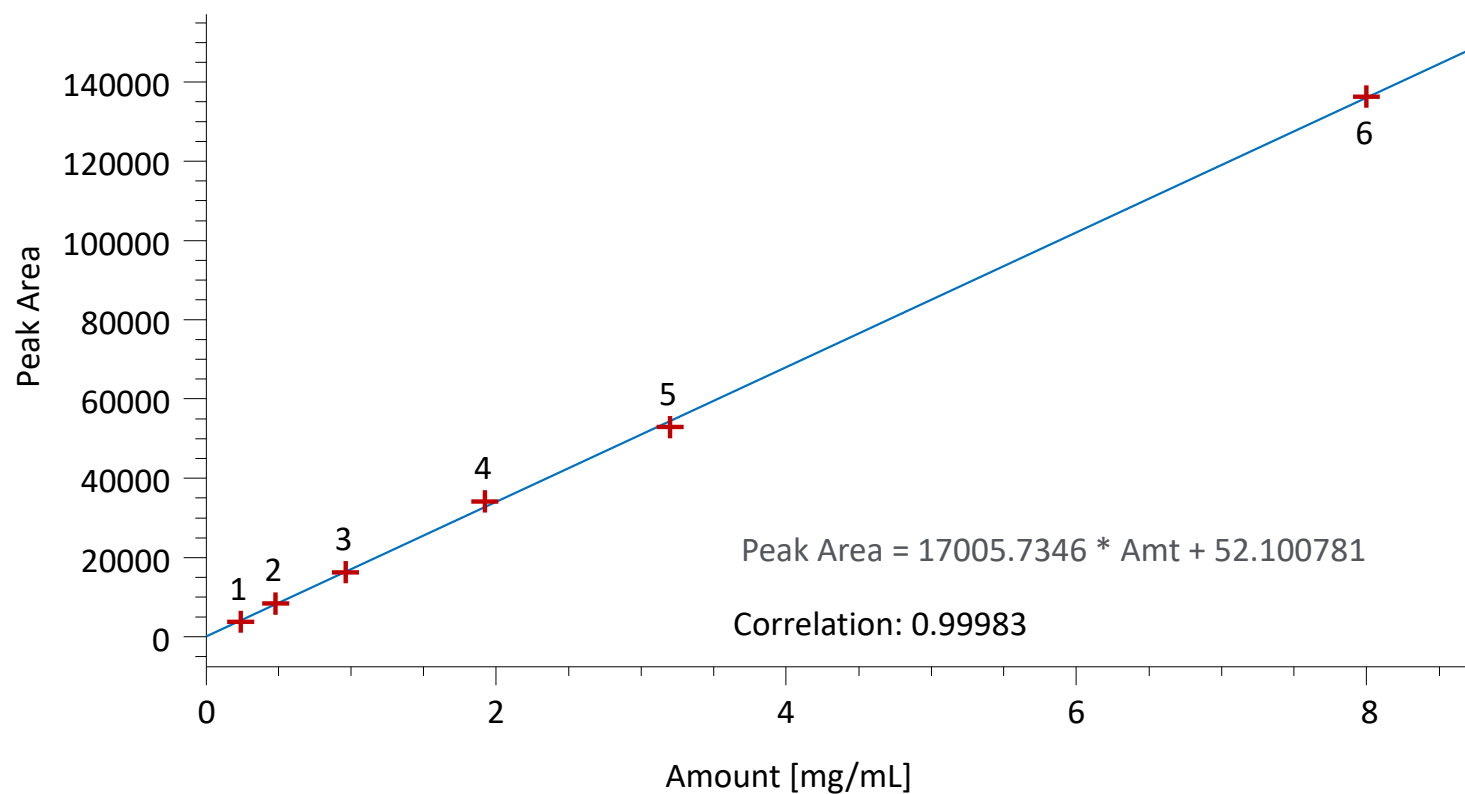
UFGC TPH Analysis in Soil – Sample Analysis Precision

BAM-U021 Certified Reference Sample
Mineral Oil Contaminated Soil

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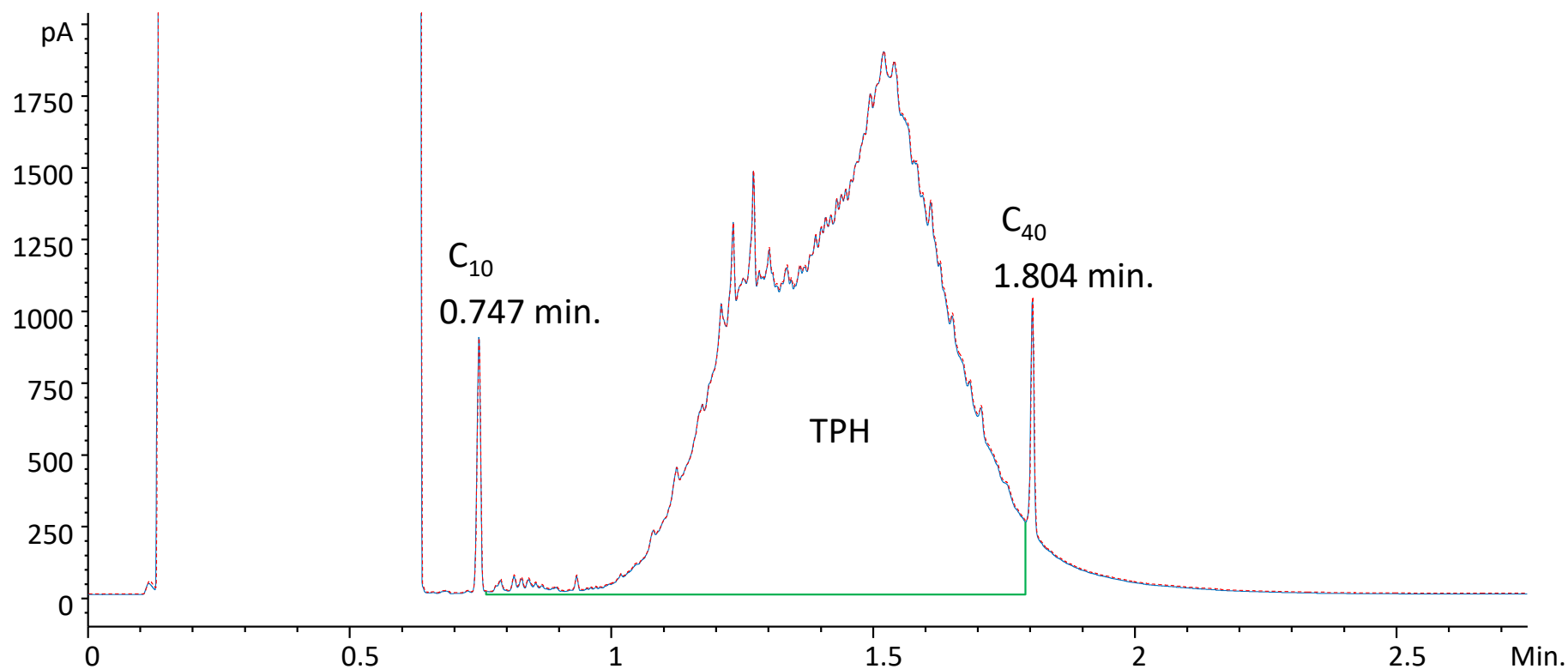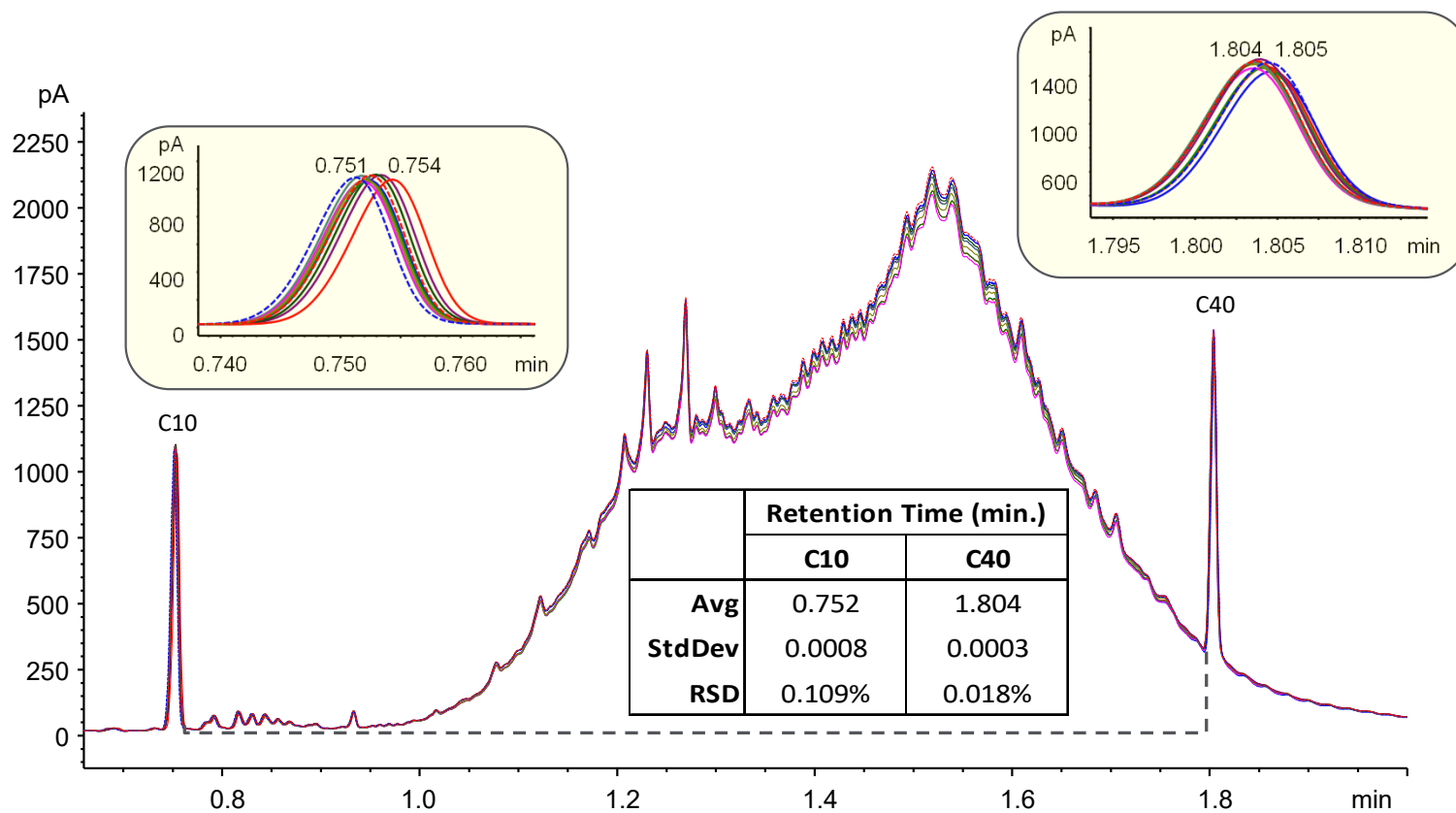
UFGC TPH Analysis in Soil – Sample Analysis Precision

	Retention Time (min.)	
	C10	**C40**
Avg	0.752	1.804
StdDev	0.0008	0.0003
RSD	0.109%	0.018%

UFGC TPH Analysis for Soil and Sediment Samples

BAM-U021
Certified Reference Sample
Mineral Oil Contaminated Soil

BAM-U022
Certified Reference Sample
Mineral Oil Contaminated Sediment

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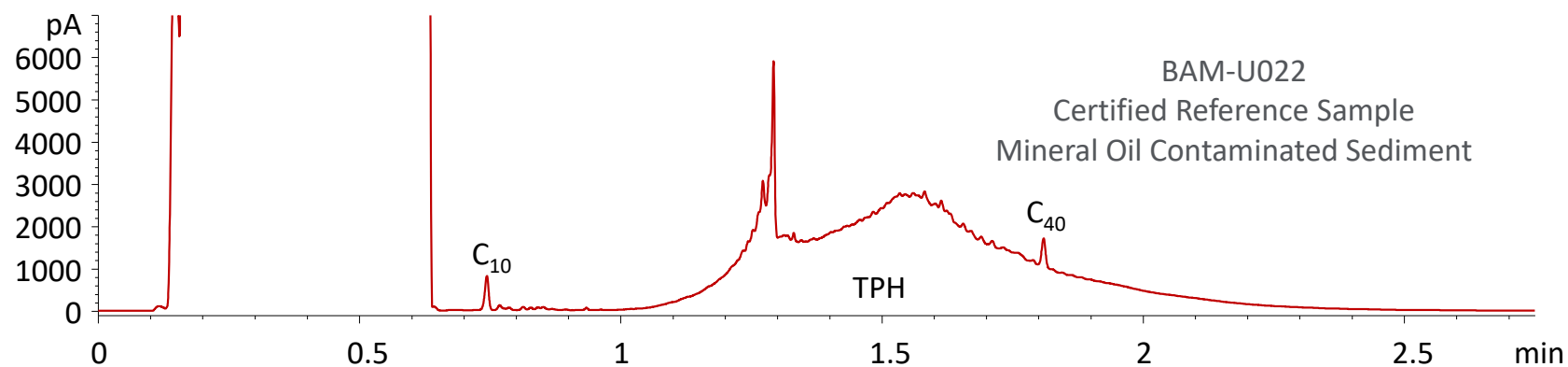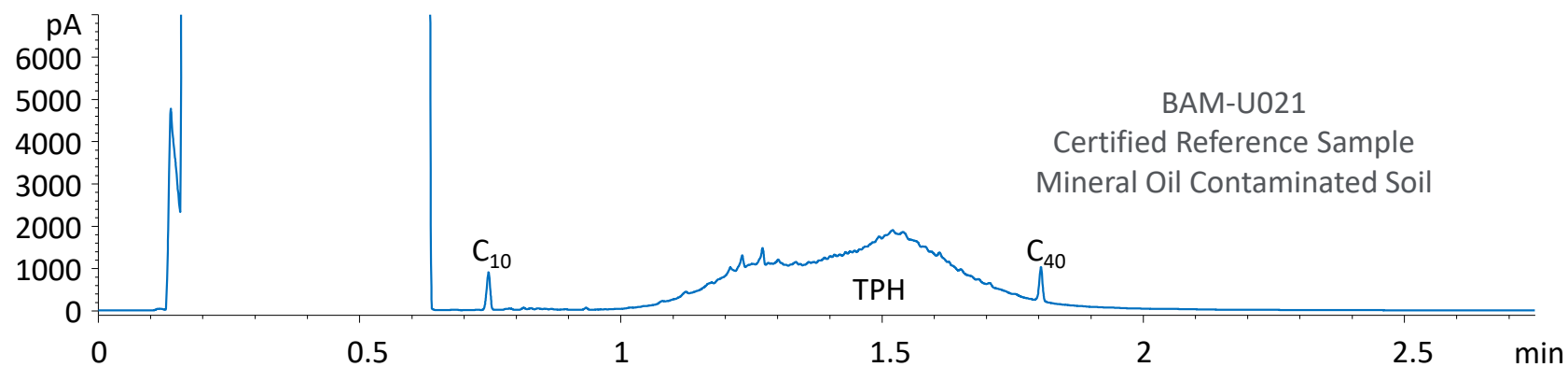
TPH Sample Performance Using UFGC Method

Run	U021 A mg/kg	U021 B mg/kg	U022 A mg/kg	U022 B mg/kg
1	3462	3480	8701	8630
2	3487	3485	8724	8658
3	3502	3482	8656	8610
4	3513	3479	8736	8732
5	3538	3492	8728	8606
Mean	**3500**	**3484**	**8709**	**8647**
Cert. Value	**3560 +/- 260**		**8270 +/- 550**	
Std Dev	**28.547**	**5.234**	**32.319**	**51.704**
RSD	**0.82%**	**0.15%**	**0.37%**	**0.60%**
r (exp)	**59**		**126**	
r* (ref)	**136**		**337**	

*r = ISO 16703 single lab precision requirement

TPH UFGC Delivers:

Method Accuracy

Instrument Precision

Method Precision

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Method Summary

- The UFGC method completes a TPH sample run in 3 minutes using short columns, fast oven programming, and high carrier gas flows

- The unique direct column heating and 6th generation EPC delivers a fast GC analysis with characteristically high retention time precision, eliminating the need for line-up manipulation of the data

- This UFGC method meets the ISO 16703 performance benchmarks for selectivity, resolution, discrimination, and calibration

- Quantitative results for certified reference samples shows extremely good agreement other labs

- Quantitative results exceed the repeatability requirements of the ISO 16703 method

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Advantages of UFGC for TPH Analysis

Lower Cost of Ownership/Return on Investment

- TPH widely run by contact labs
  - UFGC can increase sample throughput by 10x
- Greater column lifetime for UFGC methods
  - Less downtime replacing columns and re-validating method
  - Guard Chip replaces Retention Gap

Ease of Use

- Fast, easy column installation
- No complex unions or connections to make
- Guard Chip eliminates Retention Gap trimming

- Further TPH Information
  - Agilent Application Note 5991-7367EN

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