Fast GC Methods – When to Use Those Ultra-Fast Heating Rates*

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*and when not to

Innovating a New Path to GC Productivity

A whole new way to GC

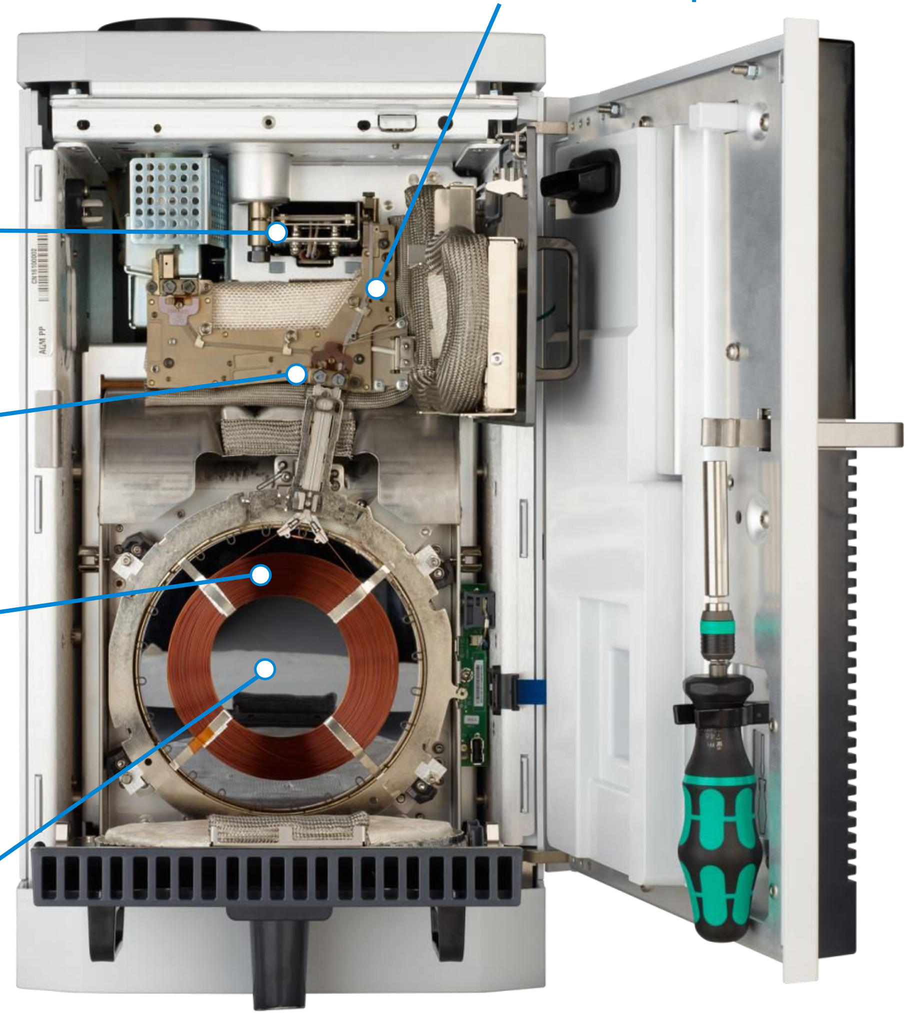
Modular
Intuvo flow chips

Disposable
Guard chip

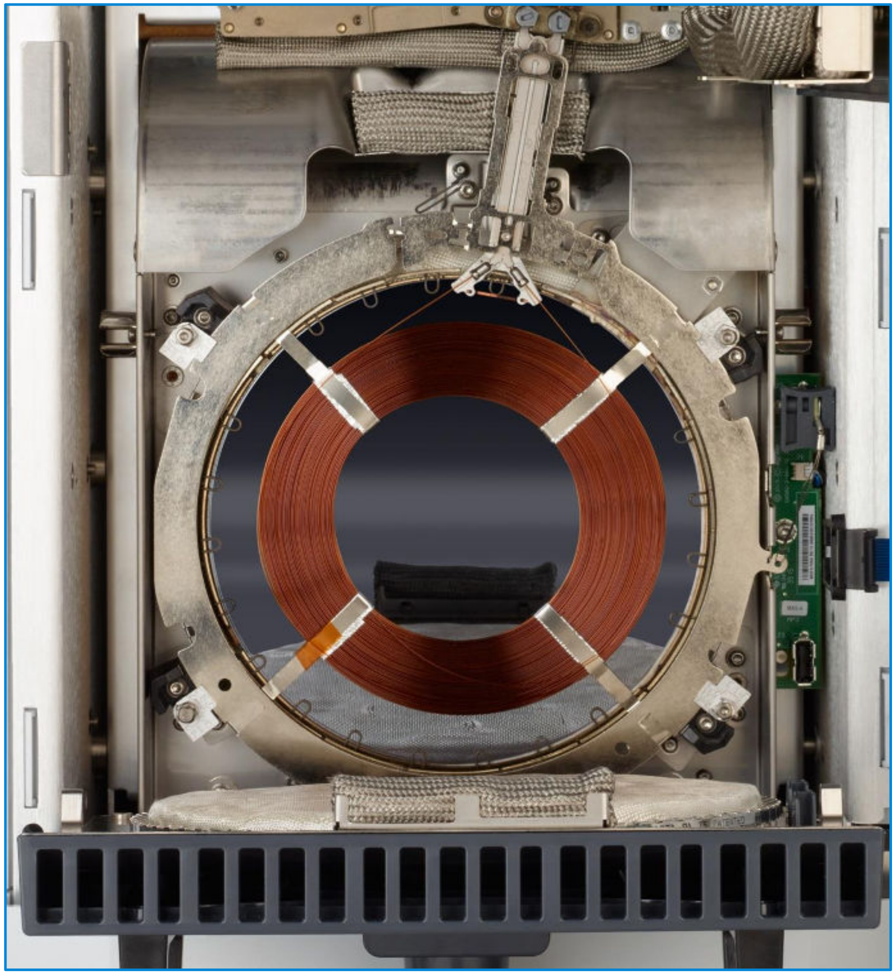
Ferrule-free click-and-run
connections

No-trim
column

Direct
heating

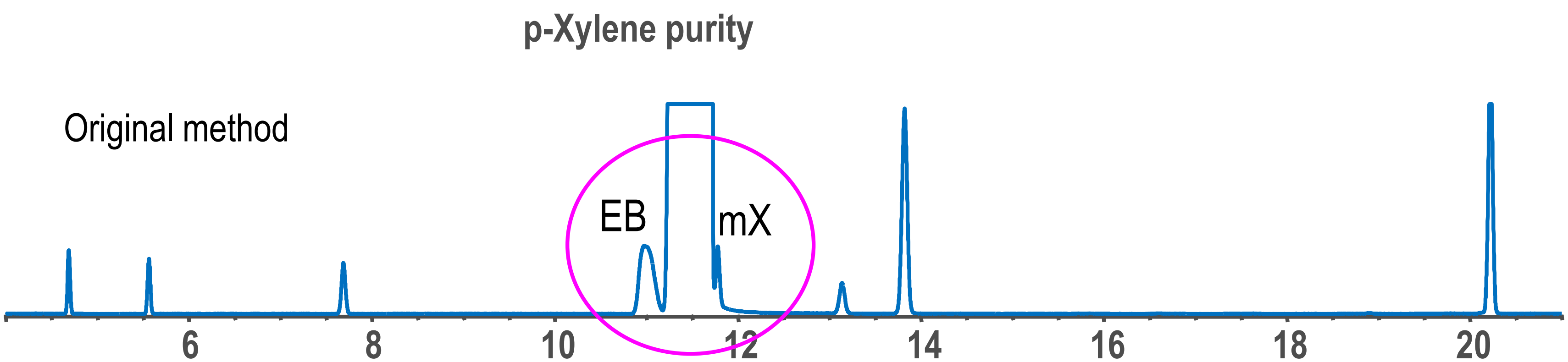


Agilent Intuvo Designed for Fast GC



- New Column Heating Technology
  - Unique approach to direct column heating
  - Fewer column elements to fail
    - no complex direct heating/sensing elements
    - no complex in-oven connections
    - Coupled to next gen EPC assures high RT precision
  - 250 ^{o}C/ min over entire oven programming range
- Ultra Fast GC Methods
  - 1 to 3 minutes run times
    - shorter, narrower columns
    - high carrier flow rates
    - >100 ^{o}C/min ramps rates

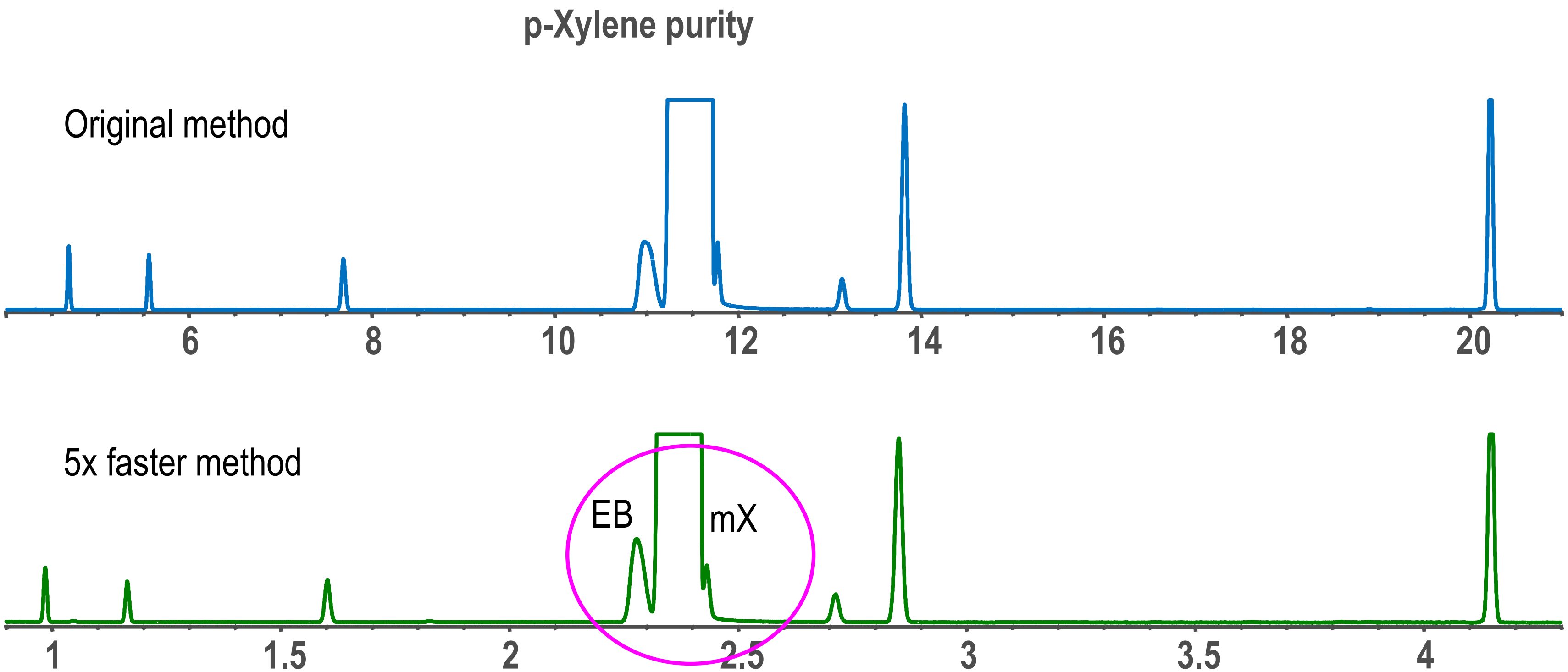
Effects of Fast Oven Ramps on Resolution



ASTM D3798 – Impurities in p-Xylene

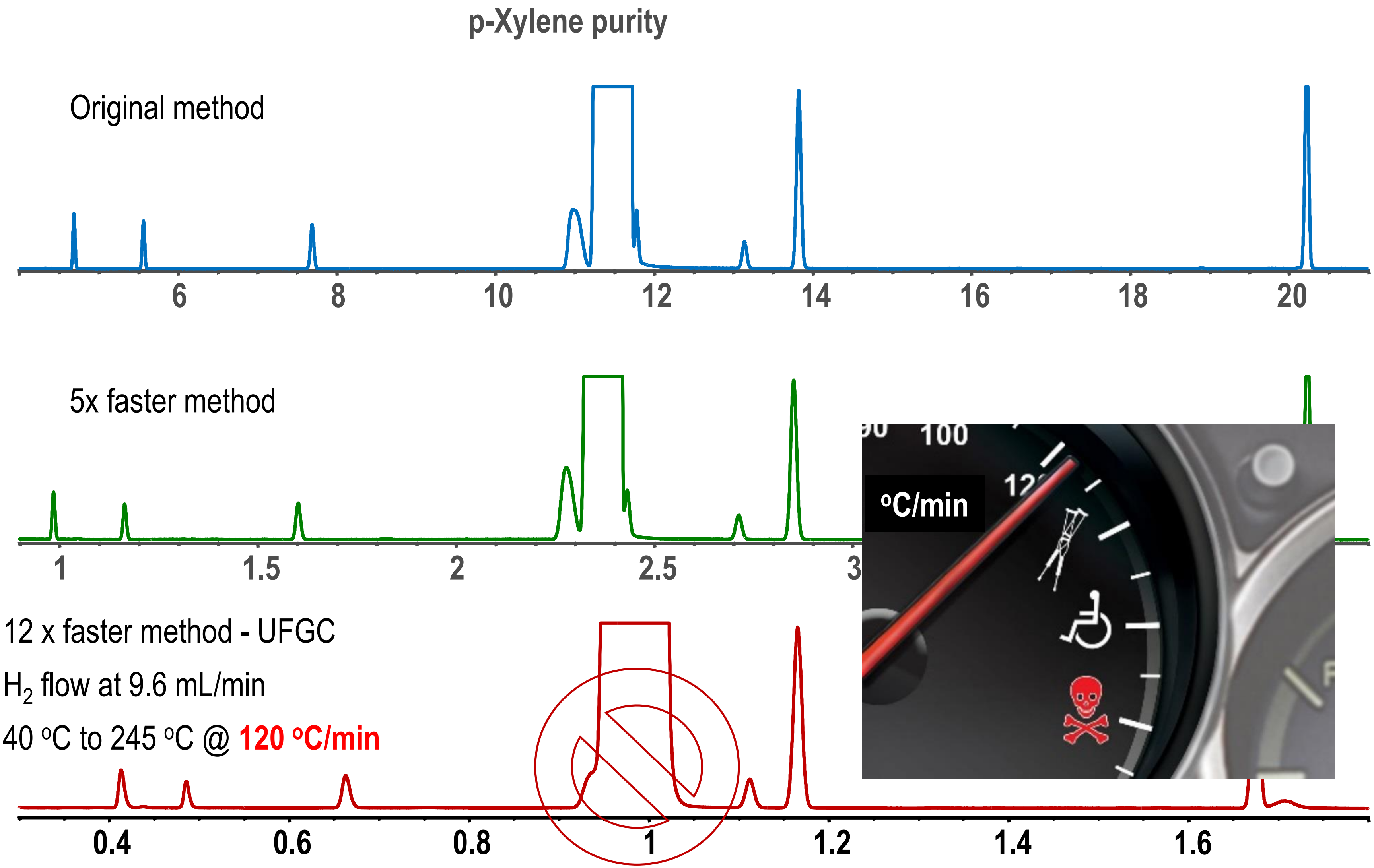
- 60 m x 0.32 mm ID x 0.5 um film wax column
- Helium flow at 2.8 mL/min
- 40 ^{o}C to 245 ^{o}C @ 10 ^{o}C/min
- Separation of ethylbenzene & m-xylene from 99% p-xylene is important

Effects of Fast Oven Ramps on Resolution



- 25 m x 0.2 mm ID x 0.25 um film wax column
- He flow at 4.4 mL/min
- 40 °C to 245 °C @ **50 °C/min**

Effects of Fast Oven Ramps on Resolution



- 12 x faster method - UFGC
- H_2 flow at 9.6 mL/min
- 40 °C to 245 °C @ **120 °C/min**

What Methods Works Best for UFGC

- Original method has lots of resolution for measured compounds or
- Little or no peak resolution is needed

- Examples
  - Simulated distillation (SimDis)
  - Total Petroleum Hydrocarbon (TPH) Analysis

ASTM D7798 – SimDis for Middle Distillates

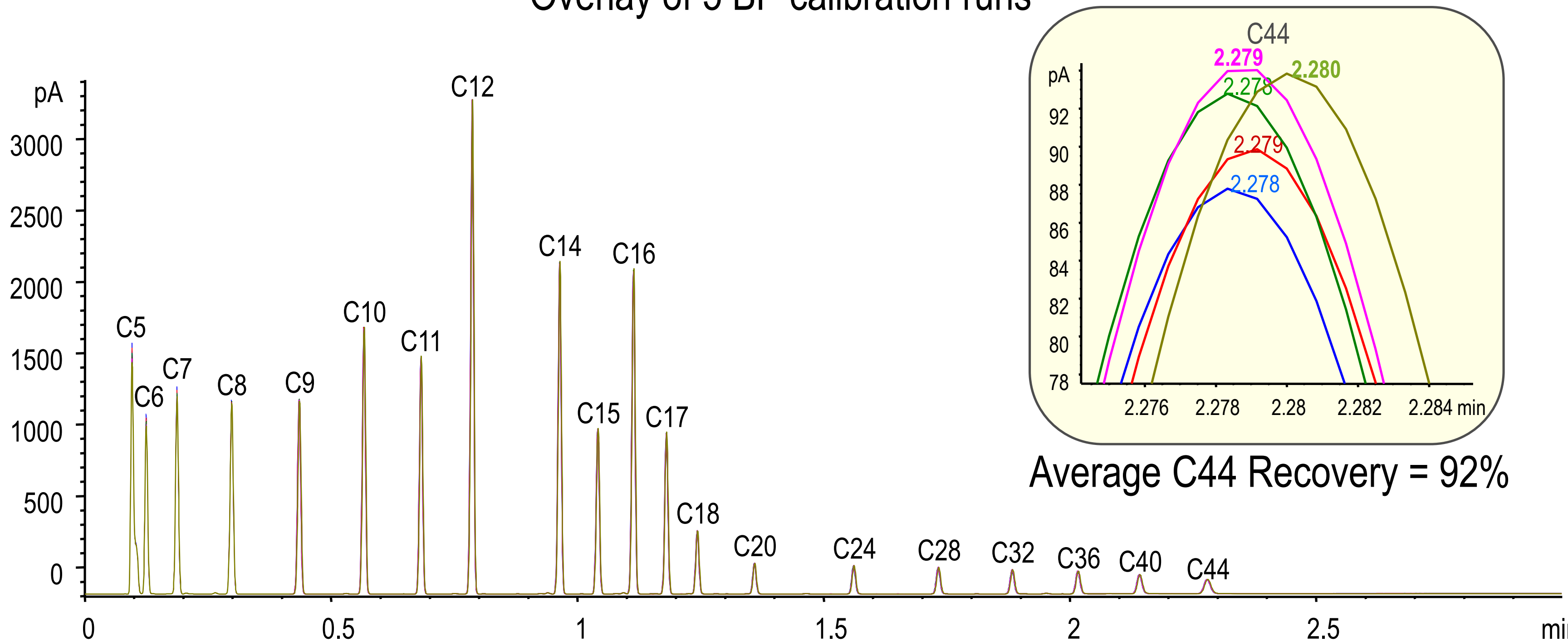
- UFGC method for the analysis of middle distillates
  - diesel, kerosene, heating oil, jet fuel
- Uses short, narrow columns with high flow rates and fast oven programming
- Run times reduced 10-fold compared to ASTM D2887

- D7798 UFGC Conditions
  - Autoinjection with 5 μL syringe, 0.1 μL injection
  - MMI Inlet, split 30:1, 5190-2293 UI liner, 350 °C
  - DB-1 column, 4 m x 0.25 mm ID x 0.25 μm
  - Helium carrier gas @ 8 mL/min constant flow
  - Oven program: 40 °C for 0 min, 160 °C/min to 350 °C, hold 1 min
  - FID, 350 °C

Challenges for UFGC When Running SimDis

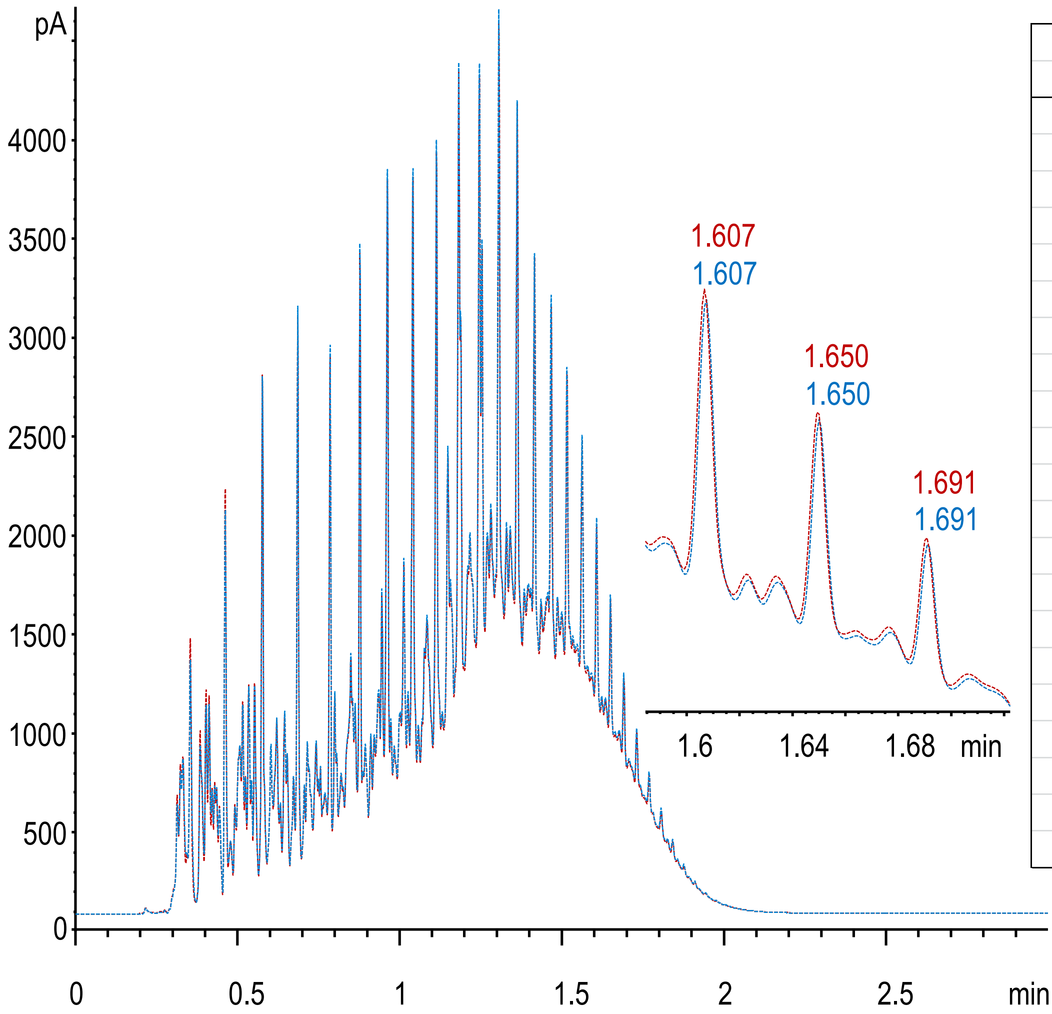
- retention time precision
  - small variations in RTs can lead to imprecise BP determination
- system discrimination
  - incomplete transfer of entire sample from inlet to detector causes failed BP cut determination

Overlay of 5 BP calibration runs



SimDis QC Sample Runs - Reference Gas Oil (RGO)

Overlay of two Intuvo RGO runs



	Ref	Allowed	RGO Start		RGO End	
	Temp (°C)	Diff (°C)	Temp (°C)	Diff (°C)	Temp (°C)	Diff (°C)
IBP	115	7.6	115	0	115	0
5	151	3.8	151	0	151	0
10	176	4.1	177	1	177	1
15	201	4.5	203	2	203	2
20	224	4.9	227	3	227	3
25	243		246		246	
30	259	4.7	262	3	262	3
35	275		277		277	
40	289	4.3	291	2	291	2
45	302		303		303	
50	312	4.3	314	2	314	2
55	321	4.3	323	2	323	2
60	332	4.3	333	1	333	1
65	343	4.3	345	2	345	2
70	354	4.3	355	1	355	1
75	365	4.3	367	2	367	2
80	378	4.3	380	2	380	2
86	391	4.3	393	2	393	2
90	407	4.3	409	2	409	2
95	428	5	430	2	430	2
FBP	475	11.8	473	2	473	2

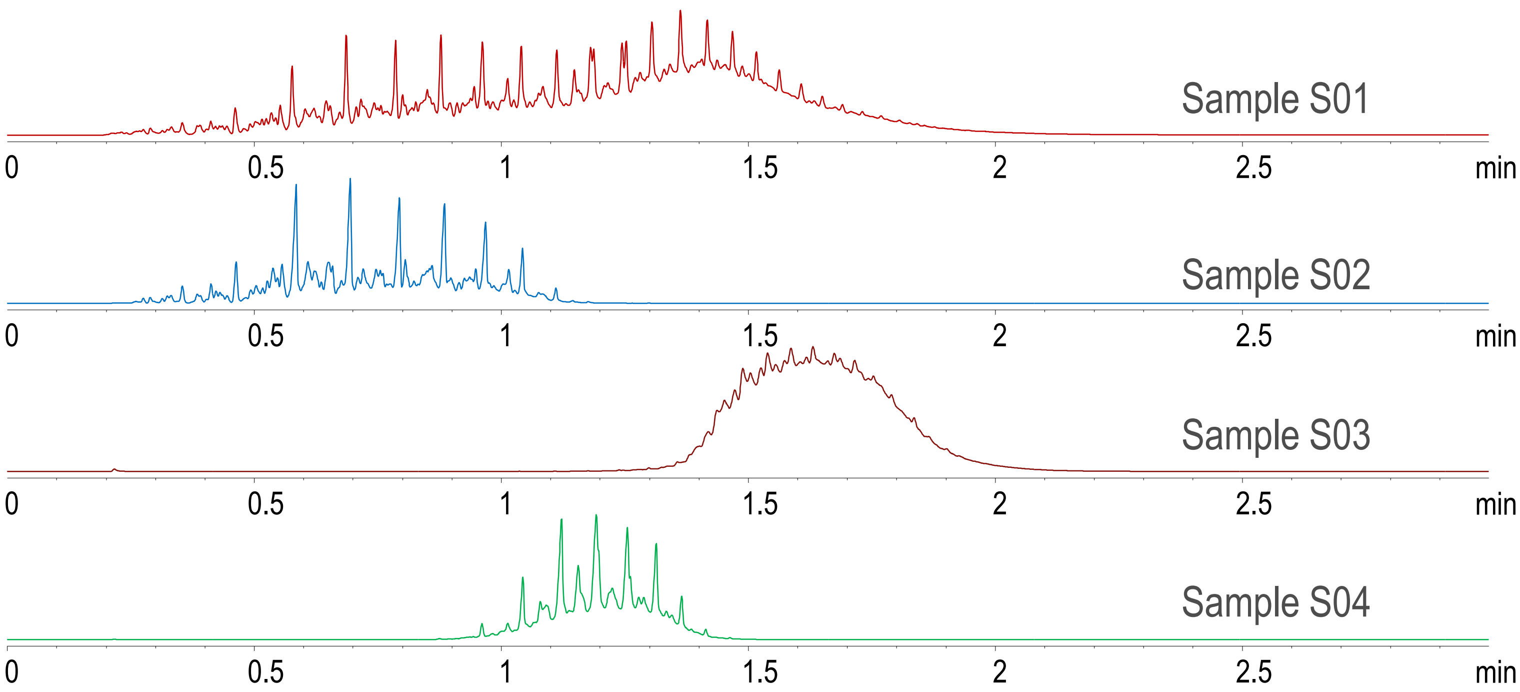
Comparing UFGC SimDis (D7798) and Conventional SimDis (D2887)

Experimental Details

- 24 middle distillate duplicates run on 7890 series GC using ASTM D2887 conditions
- Same samples run on Intuvo GC using ASTM D7798 conditions
- Instrument blanks run before and after sample set to assure consistent baseline and no carry-over
- QC sample (reference gas oil) run before and after sample set to assure system performance

% Off	Temperature (deg. C)							
	Sample 01		Sample 02		Sample 03		Sample 04	
	D2887	D7798	D2887	D7798	D2887	D7798	D2887	D7798
IBP	119	117	107	104	331	336	246	247
5	174	174	146	145	360	362	268	269
10	198	198	162	163	368	370	275	276
15	217	218	169	170	374	376	282	282
20	235	236	175	176	379	381	288	288
25	252	253	180	181	385	387	290	290
30	268	270	186	188	389	391	294	295
35	284	286	193	195	394	396	298	298
40	298	301	198	198	398	400	302	303
45	310	313	202	204	403	405	305	305
50	321	324	209	211	407	409	307	307
55	331	334	217	217	411	414	310	311
60	341	344	219	221	416	419	313	314
65	349	353	227	229	420	423	317	319
70	358	361	233	235	425	428	320	320
75	367	370	237	239	430	433	323	325
80	376	380	246	247	435	439	327	329
86	389	392	253	254	441	445	332	333
90	404	408	259	262	449	452	335	338
95	428	431	271	272	461	464	344	346
FBP	481	481	290	290	490	490	363	365

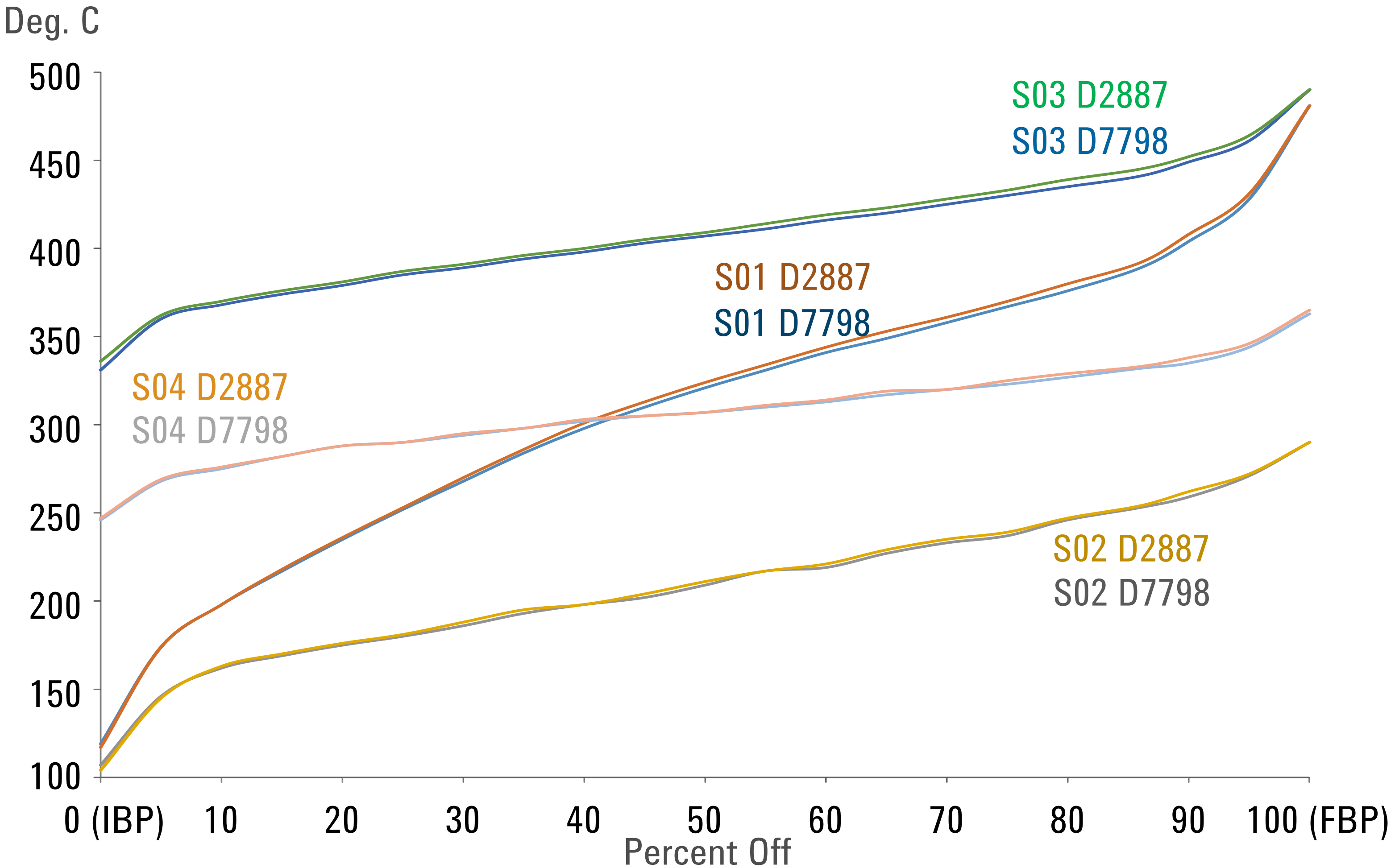
UFGC SimDis Sample Runs



Four different sample types

- S01 – wide boiling range
- S02 – narrow, lower boiling range
- S03 narrow, high boiling
- S04 – narrow, mid boiling range

Comparing UFGC SimDis (D7798) and Conventional SimDis (D2887)



GC Conditions for UFGC TPH Analysis

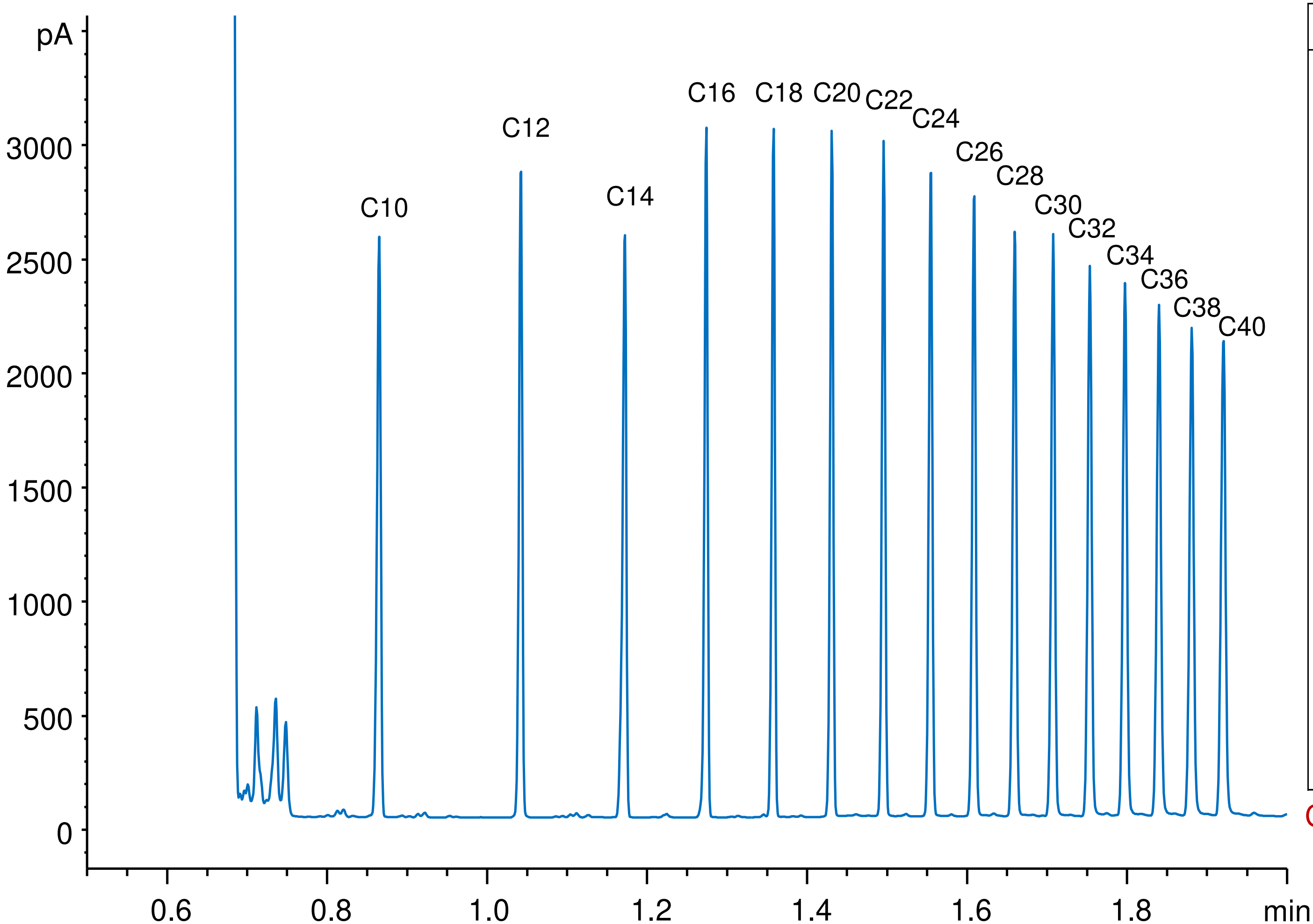
Intuvo GC Conditions:

- ALS with 10 µL syringe, 1 µL injection
- SSL Inlet, splitless mode, 5190-2293 UI liner, 400 °C
- Guard Chip, oven track mode
- DB-5ht column, 5 m x 0.32 mm ID x 0.1 µm
  - helium carrier gas @ 10 mL/min constant flow
  - oven program, 40 °C for 0.5 min, 250 °C/min to 350 °C, hold 0.5 min
- FID, 350 °C

TPH Samples - Certified Reference Materials from Bundesanstalt für Materialforschung und –prüfung (BAM)

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

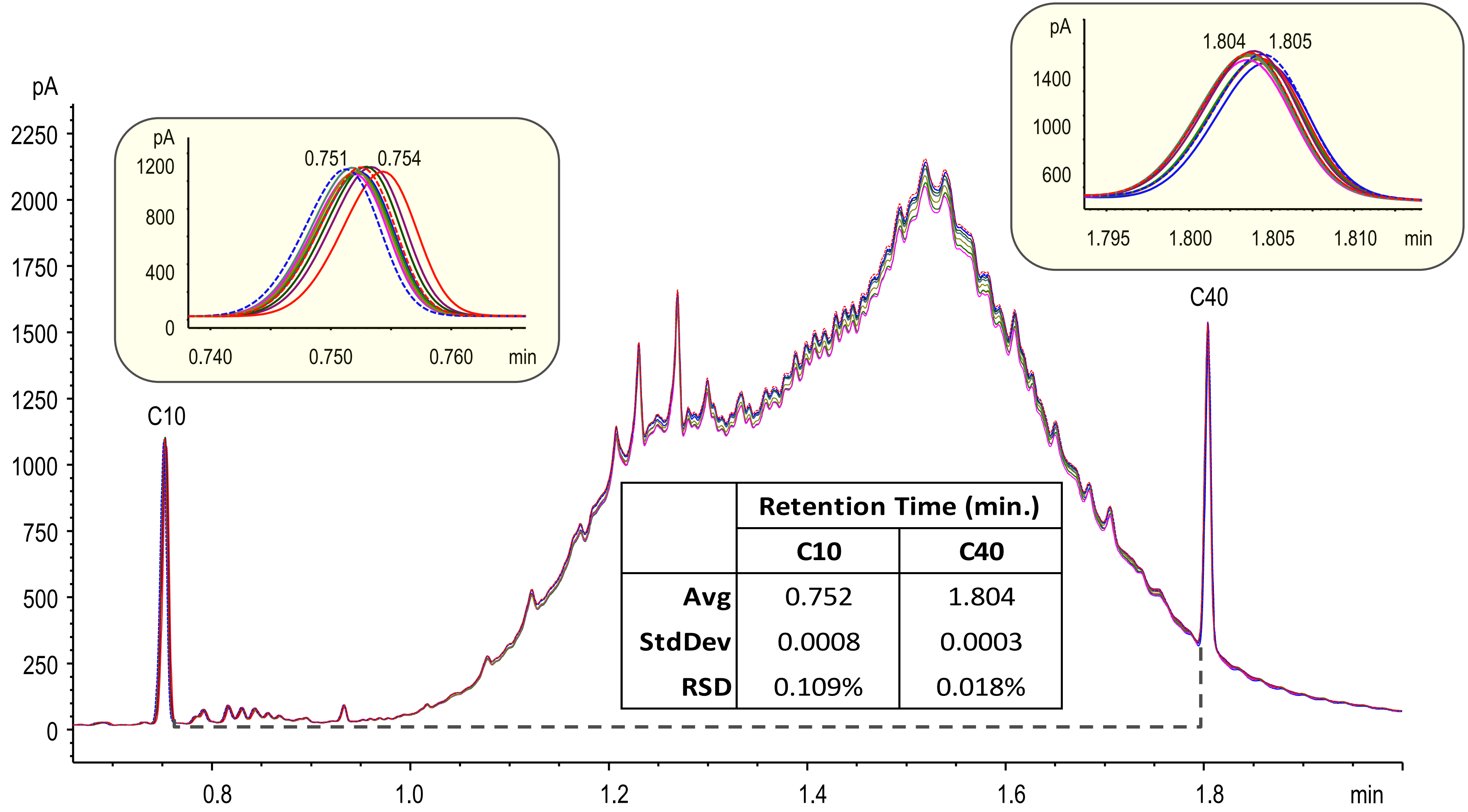
UFGC TPH Discrimination Performance Test



	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

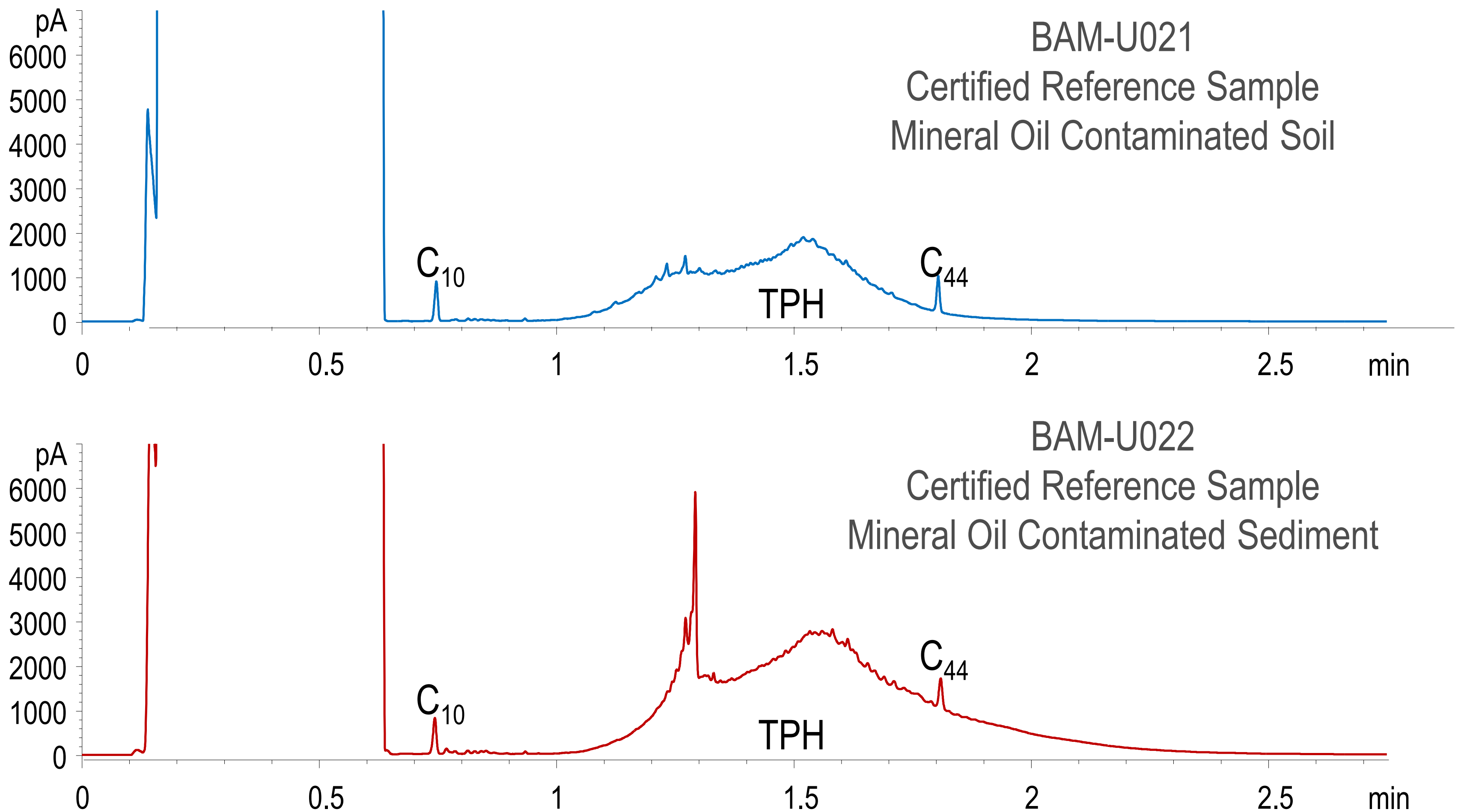
C40 recovery must be > 0.80

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



TPH Sample Performance Using Intuvo UFGC

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**	

Method Accuracy

Instrument Precision

Method Precision

*r = ISO 16703 single lab precision requirement

Conclusions

- A new technology for fast capillary column heating uses a direct heating disk to rapidly transfer heat to a planar capillary GC column.
- This enables fast and precise column heating up to 250 ^{o}C across the a temperature range of 40 ^{o}C to 450 ^{o}C.

- Extremely fast temperature programming is ideal for minimizing GC analysis times when individual peak resolution is not required.
- High retention time precision and low boiling point discrimination assured precise and reliable results.