

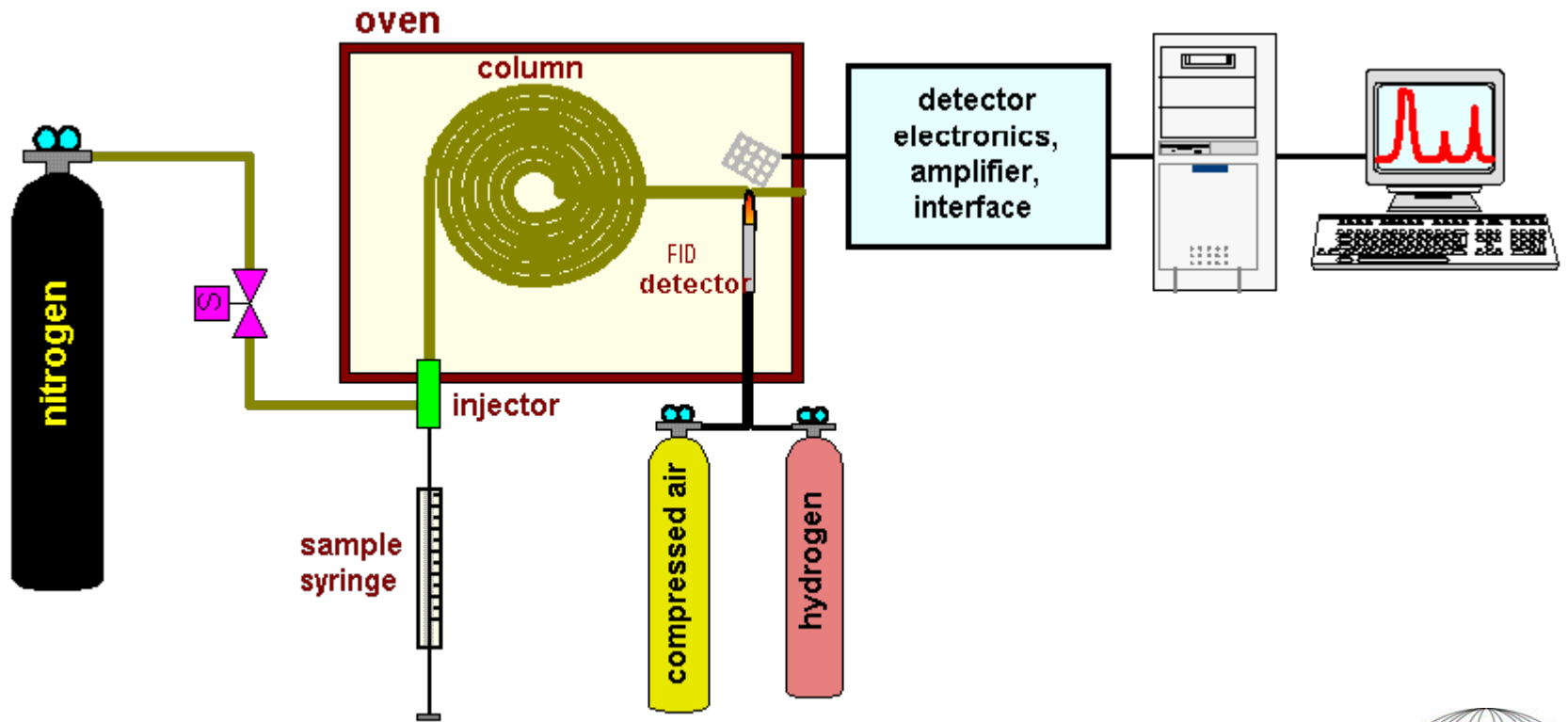
Approaches to quantify the biogenic interference on Petroleum hydrocarbon levels

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Remtech 2007

Outline

- GC/FID hydrocarbon analysis
- Silica gel treatment
- Approaches to quantify the biogenic interference

Gas Chromatography



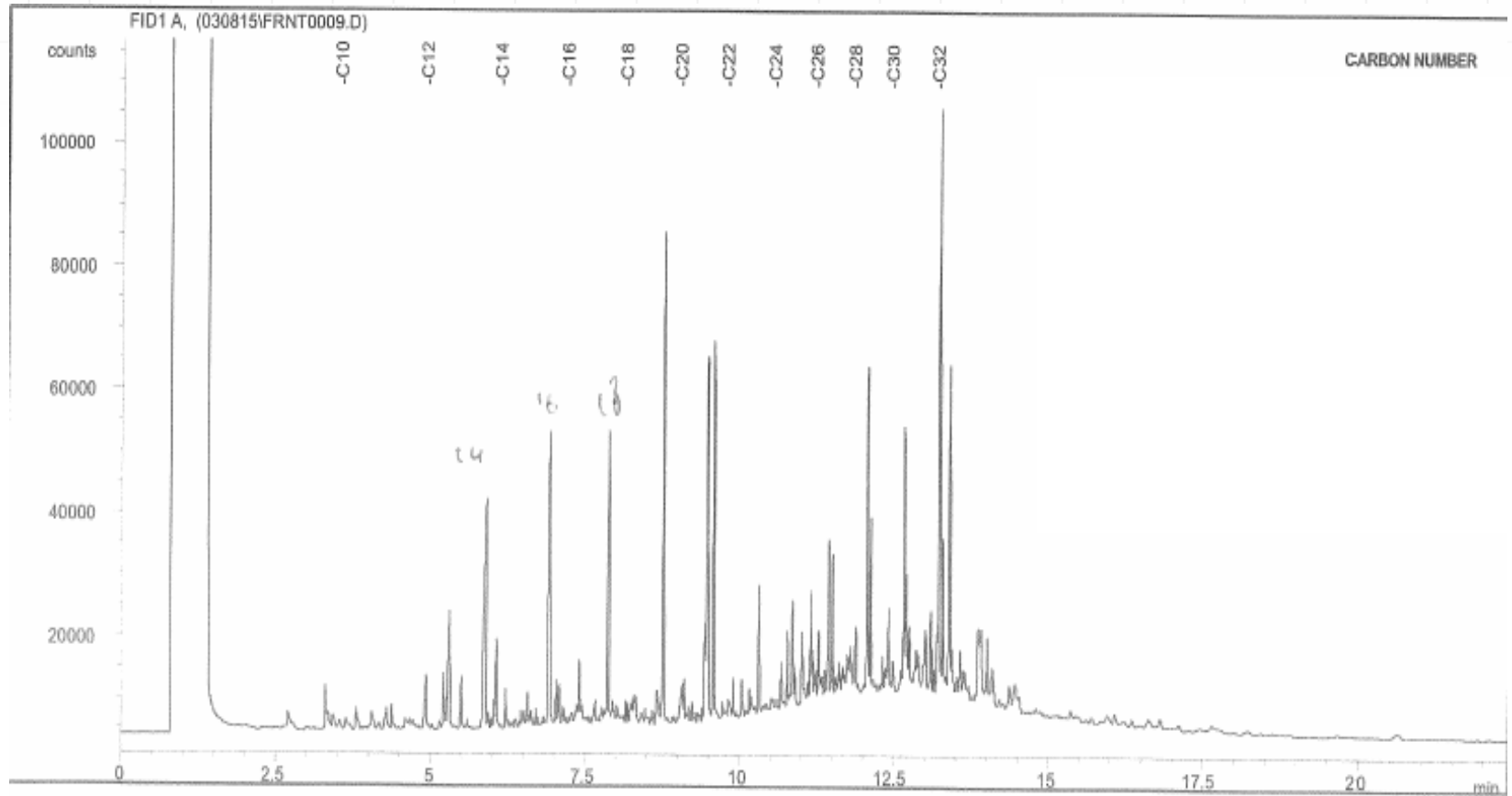
Hydrocarbon Analysis

- Developed to provide quantitative information. Example - for regulatory decisions
- CCME method provides some characterization – hydrocarbon ranges.
- Information about composition of the hydrocarbon is not provided.
- Methods are not capable of distinguishing between materials with similar properties.

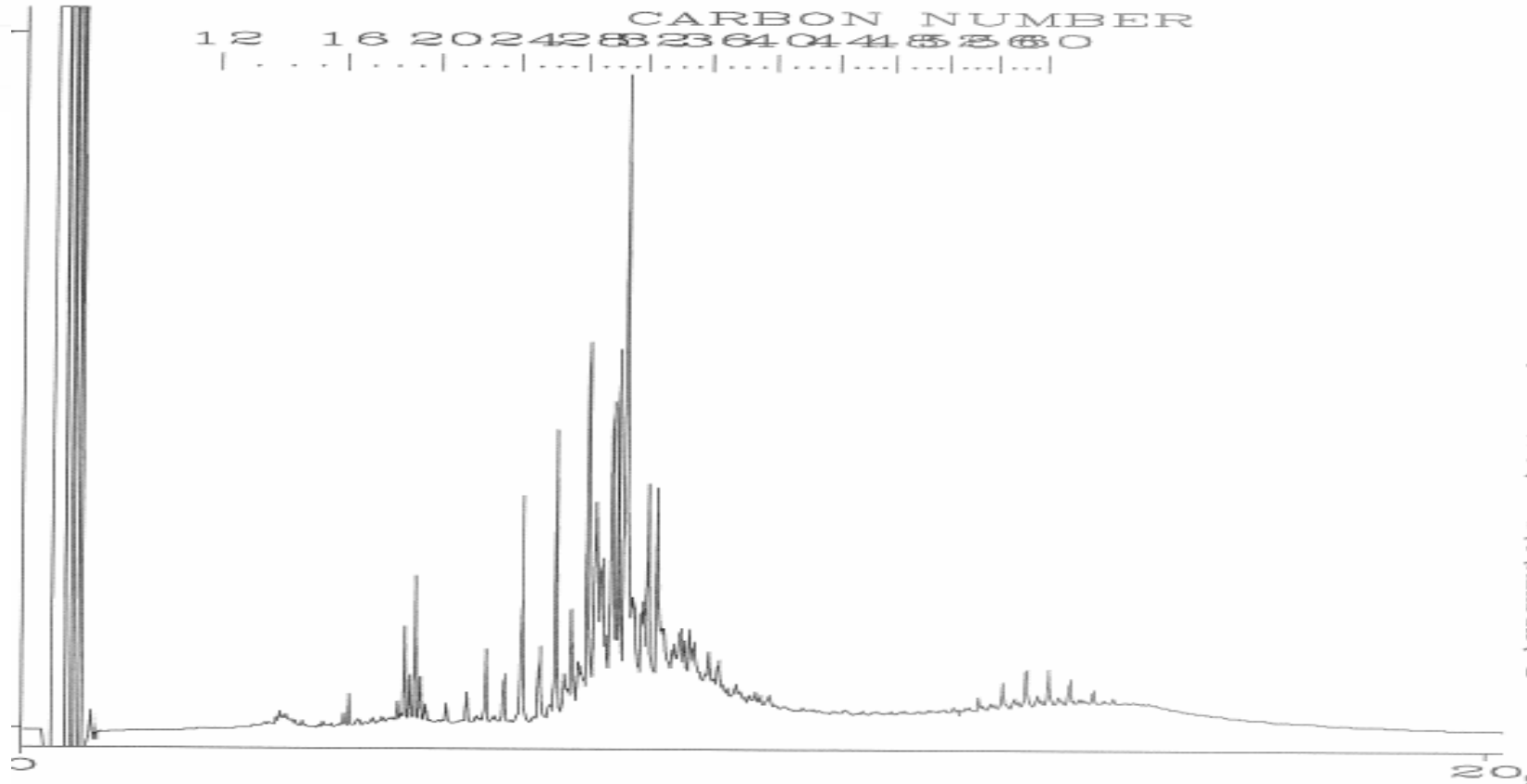
Organic compounds detected by GC/FID

- Volatile aromatics (BTEX)
- Polyaromatic hydrocarbons (PAHs)
 - Alkylated PAHs
 - Hetero PAHs (S and N)
- Waxes and Asphalthenes
- Organic acids (fatty acids)

Farm soil



Plant material



Biogenic Hydrocarbons

- Odd carbon-numbered n-alkanes are much abundant than even carbon-numbered n-alkanes in the C21- C33 range.
- Note absence of UCM;
- Presence of "biogenic cluster" in the GC.

Peat- extracted

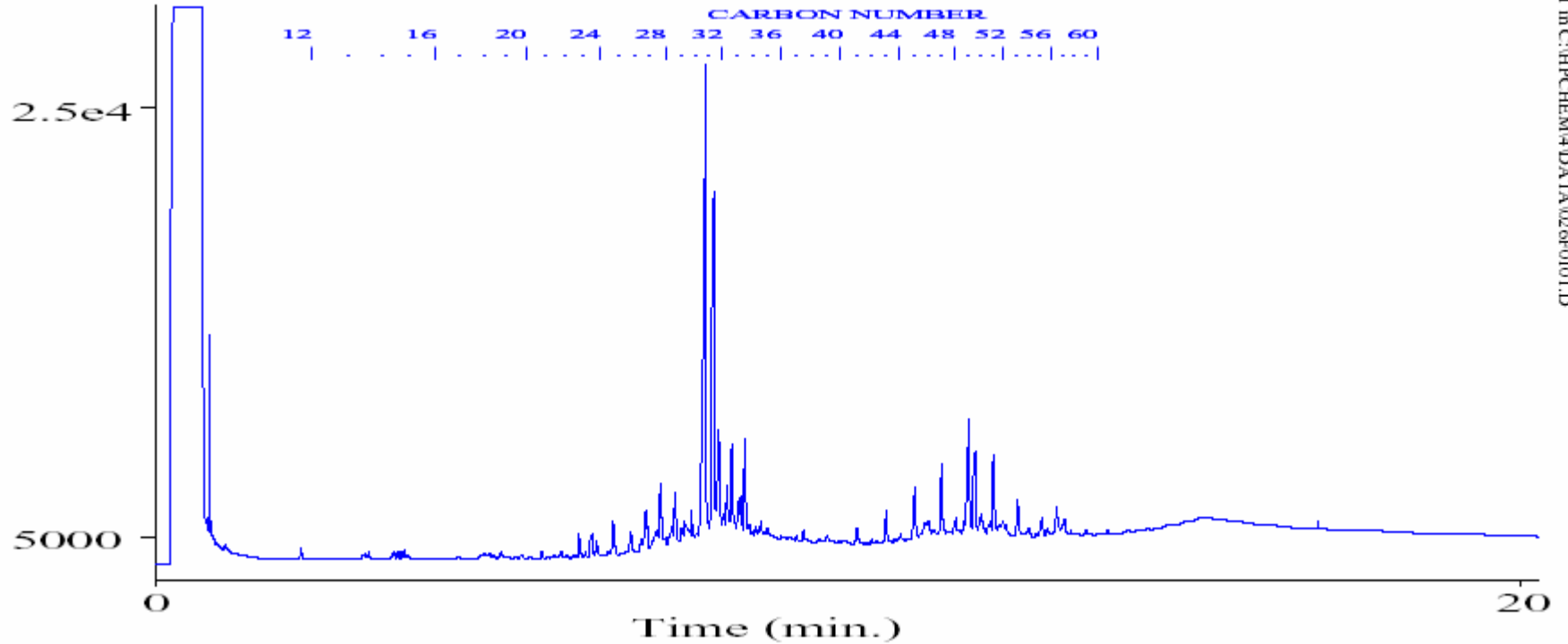


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CCME

Summary of Tier I Levels (mg/kg) for surface soil.

Land Use	Soil Texture	Fraction 1 C6-C10		Fraction 2 C10-C16		Fraction 3 C16-C34		Fraction 4 C34+
		2007	old	2007	old	2007	old	Old/new
Agricultural	Coarse-grained	30	130	150	450(90)	300	400	2800
	Fine-grained	210(170)	260(180)	150	900(250)	1300	800	5600
Residential/ Parkland	Coarse-grained	30	30	150	150(90)	300	400	2800
	Fine-grained	210(170)	260(180)	150	900(250)	1300	800	5600
Commercial	Coarse-grained	320(240)	310(300)	260	760(90)	1700	1700	3300
	Fine-grained	320(170)	660(180)	260(230)	1500(250)	2500	2500	6600
Industrial	Coarse-grained	320(240)	310(300)	260	760(90)	1700	1700	3300
	Fine-grained	320(170)	660(180)	260(230)	1500(250)	2500	2500	6600

Values in brackets for fractions 1 and 2 considers additional potable groundwater protection
For complete levels, consult Tables in the Technical Supplement Document

Interference with CCME fractions

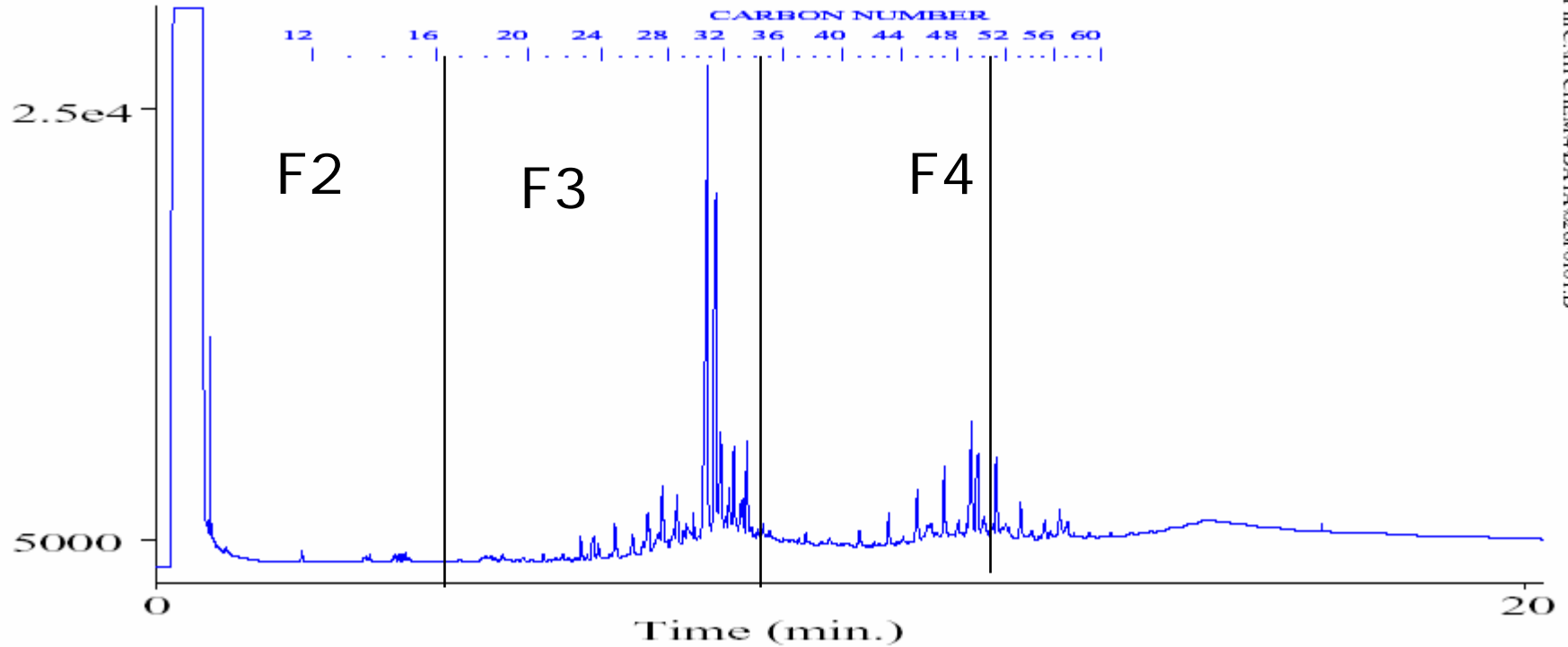


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Soxhlet (CCME)

- 20-30 gm (CCME \geq 5 gm)
- Mix with drying agent
- 16-24 hr. Soxhlet with Hexane / Acetone
- Cleanup
- Concentrate
- Assess

Soxhlets



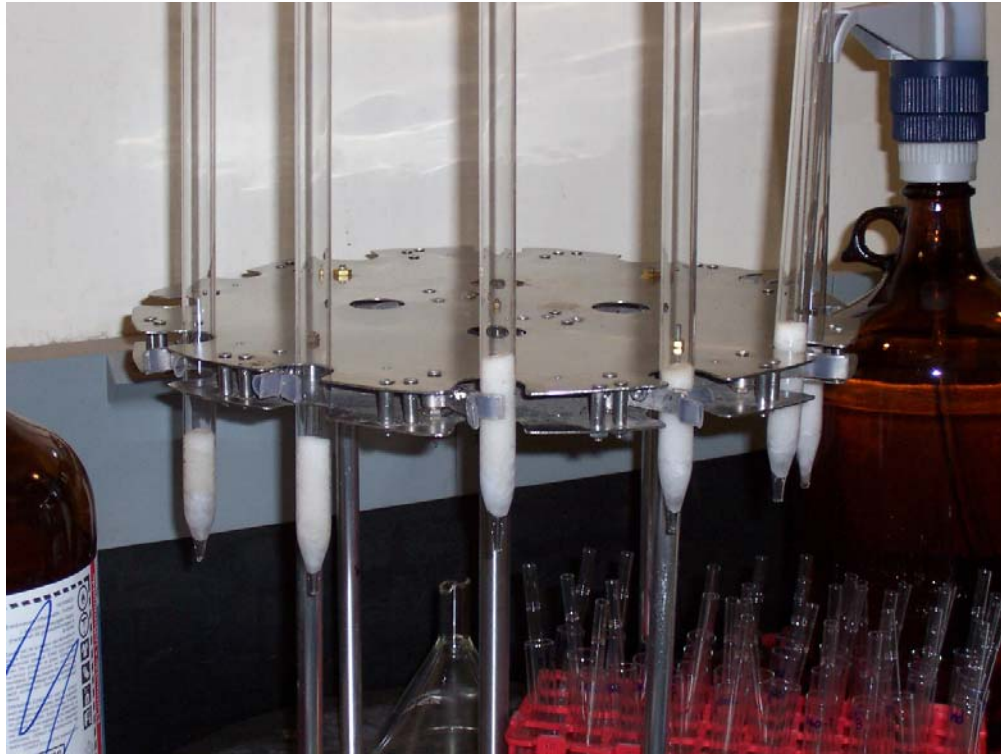
Rotatory evaporator



Concentrated Soxhlet extracts



Silica gel cleanup



GC vials



High temp GC/FIDs



C10-C60 Assessment

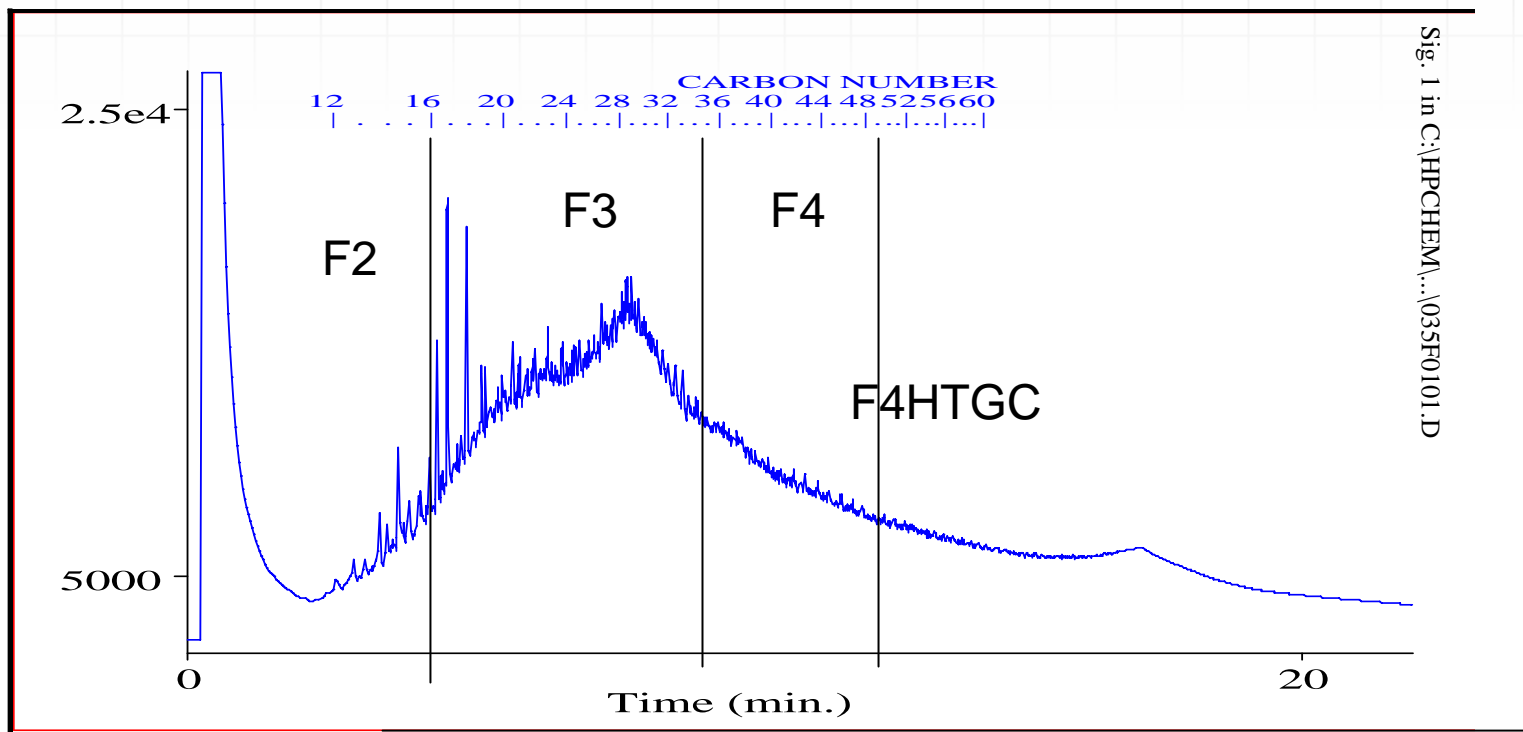
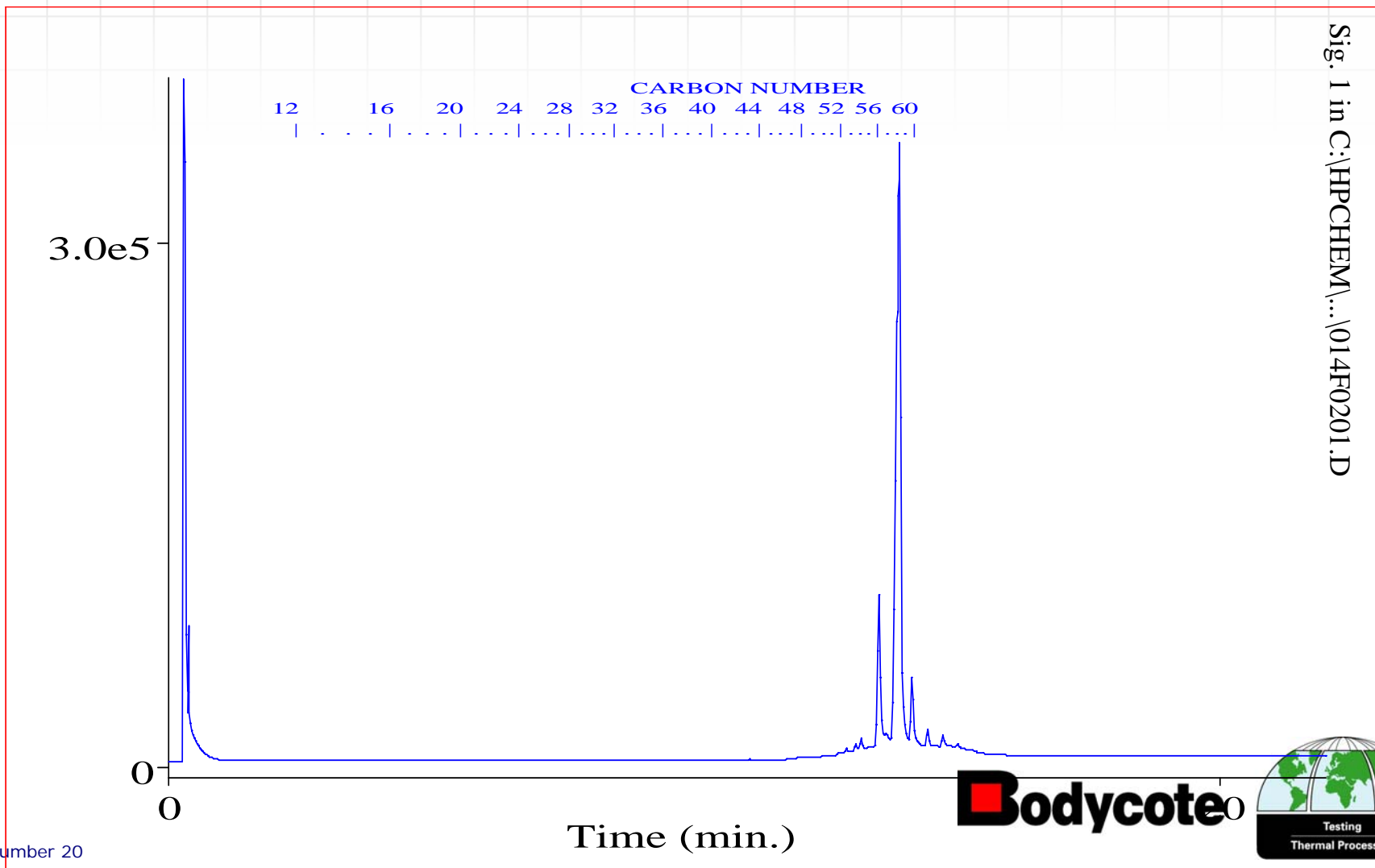


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Pure Canola Oil



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Canola and crude oil

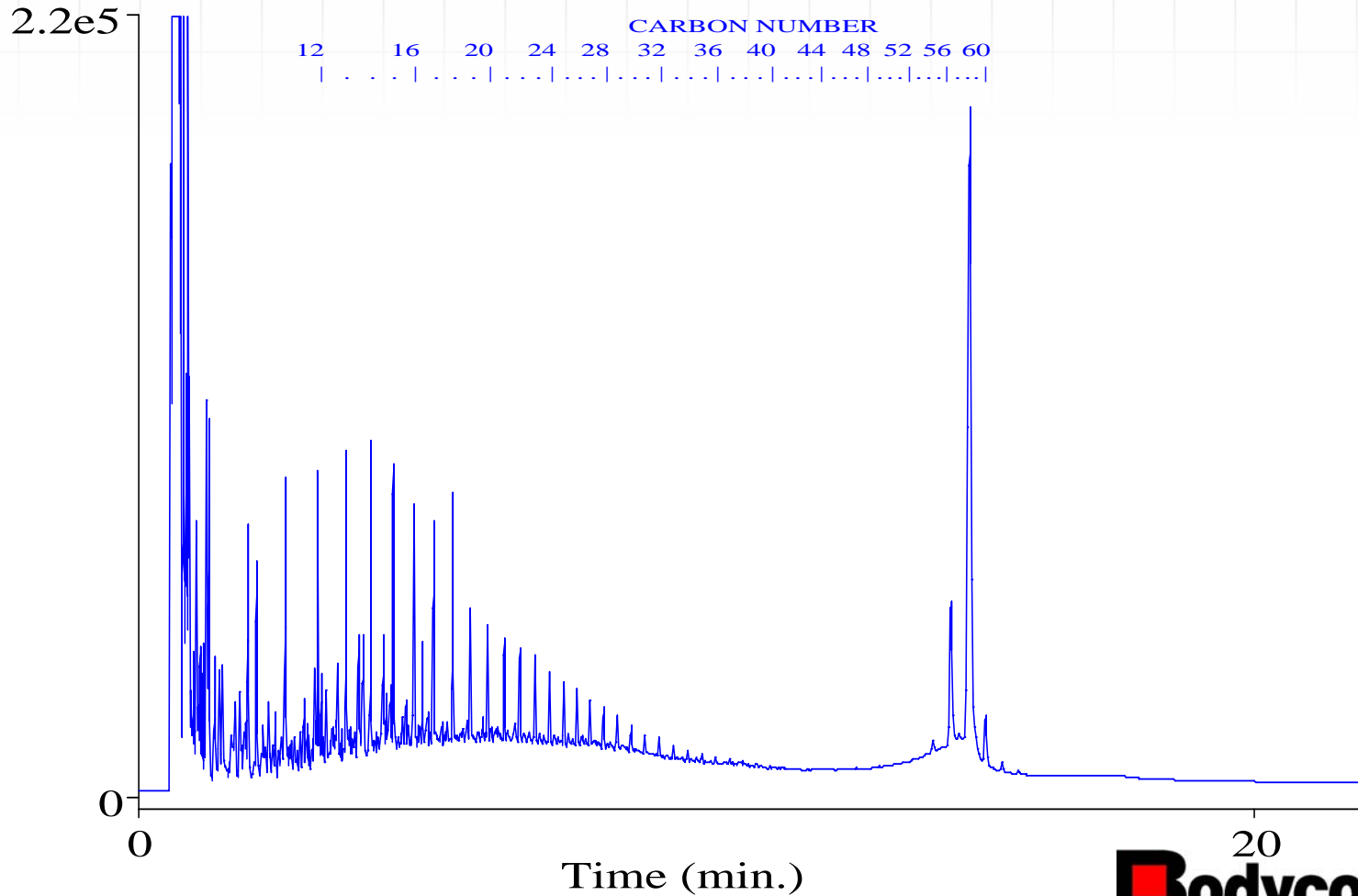
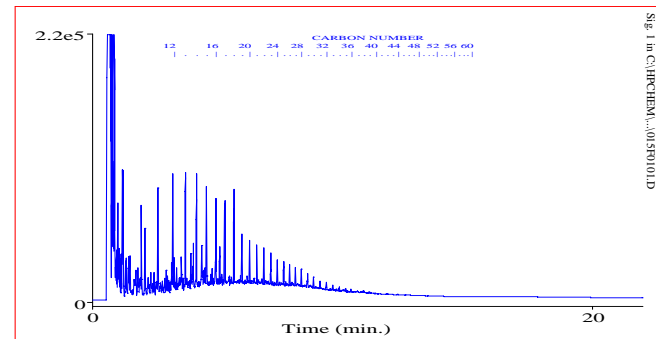
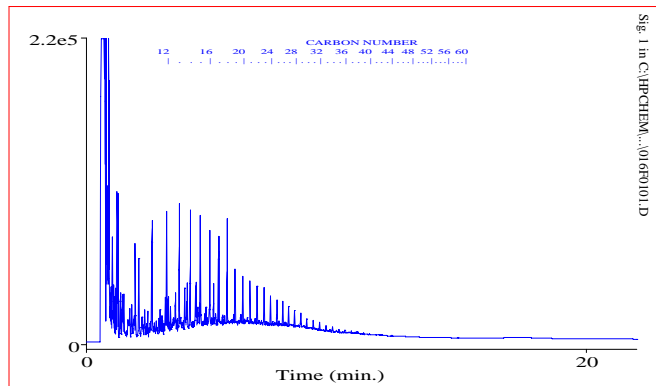
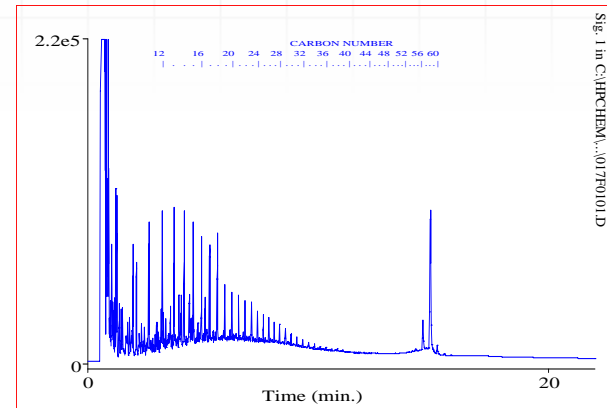
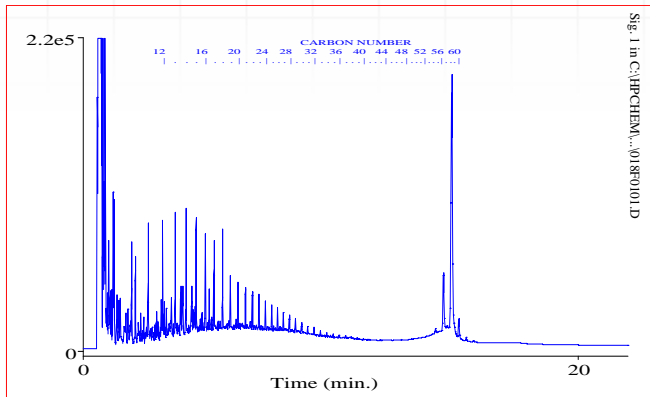


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Canola oil Removal



Silica gel treatment

➤ Losses with each treatment

fraction	% Change
	Before/after batch
F2	16 %
F3	13 %
C34-C50	1 %
C50+	30%

Natural Interferences - Peat

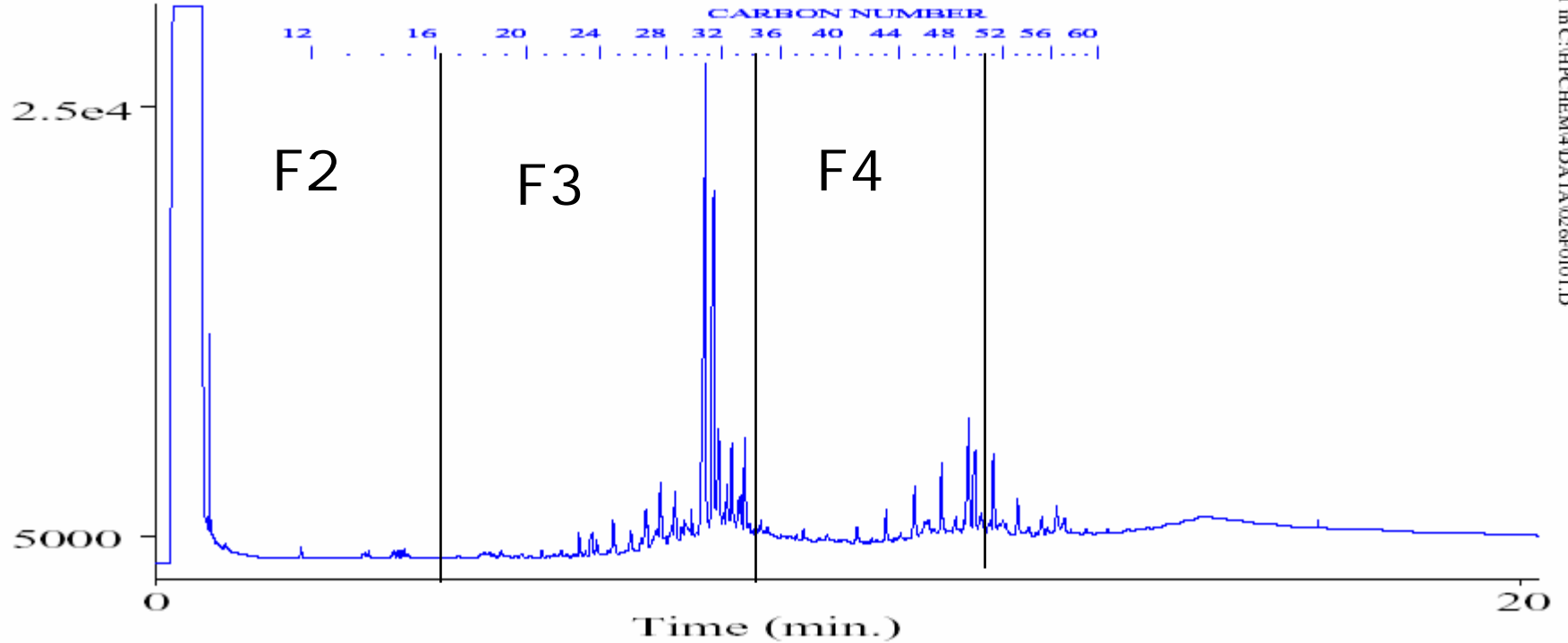
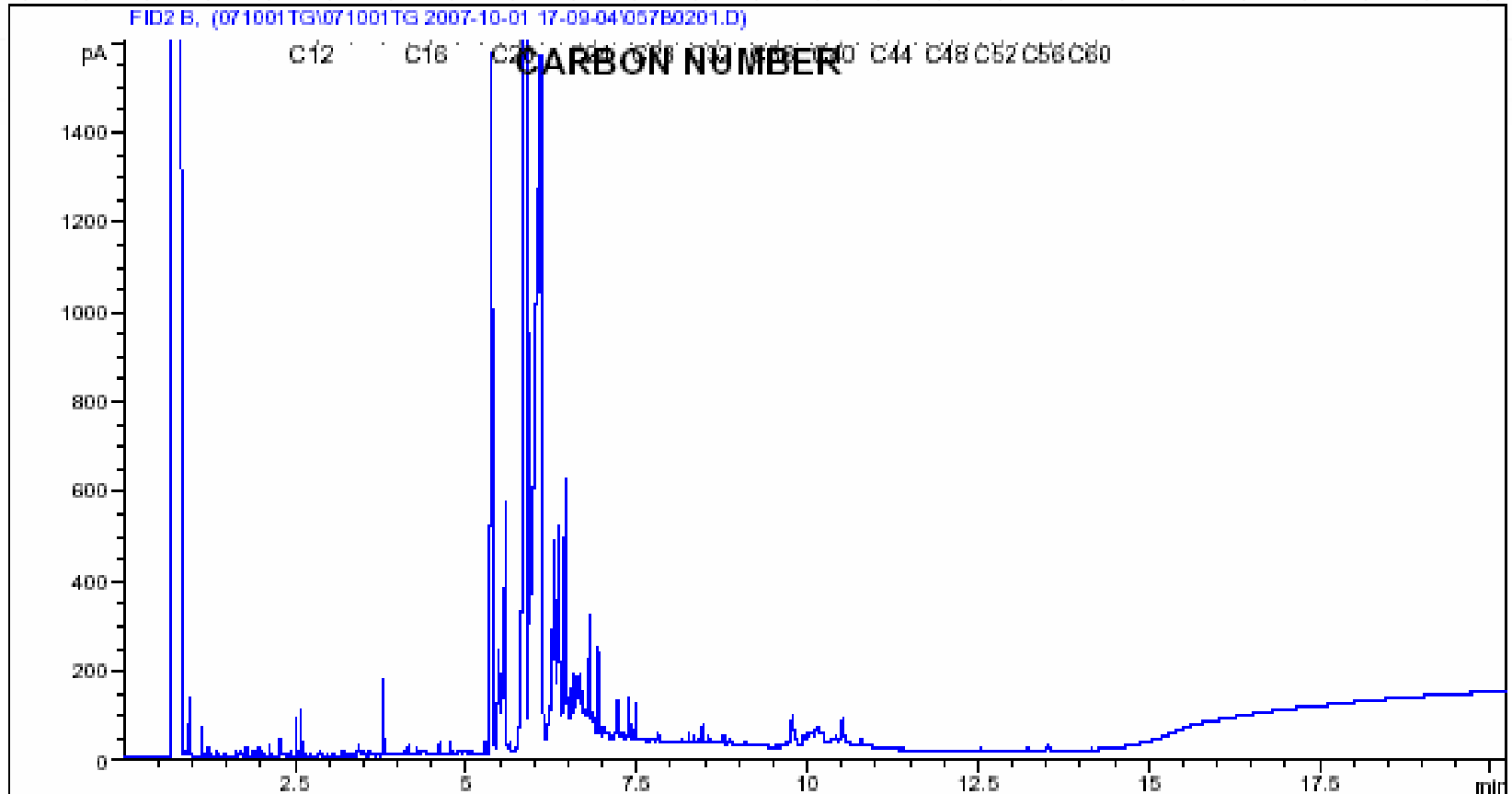


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Biodiesel waste water



Biogenic material

- Biogenic interference and silica gel Cleanup
- Tundra peat
- False positives

Conceptual Model

➤ $TEH = TPH + TOM$

$TPH = TEH - TOM$

➤ TEH from CCME fractions F2 - F4

➤ TOM from ?

➤ TPH is then the true petroleum hydrocarbons

TOM Approaches

- Blanks
- Chromatographic separation
- GC/MS
- Standard additions
- TOC + silica gel

Blank Subtraction

- Run 1: blank/amendments
- Run 2: sample
- Result: $TPH = \text{sample} - \text{blank}$

Coal in this sample

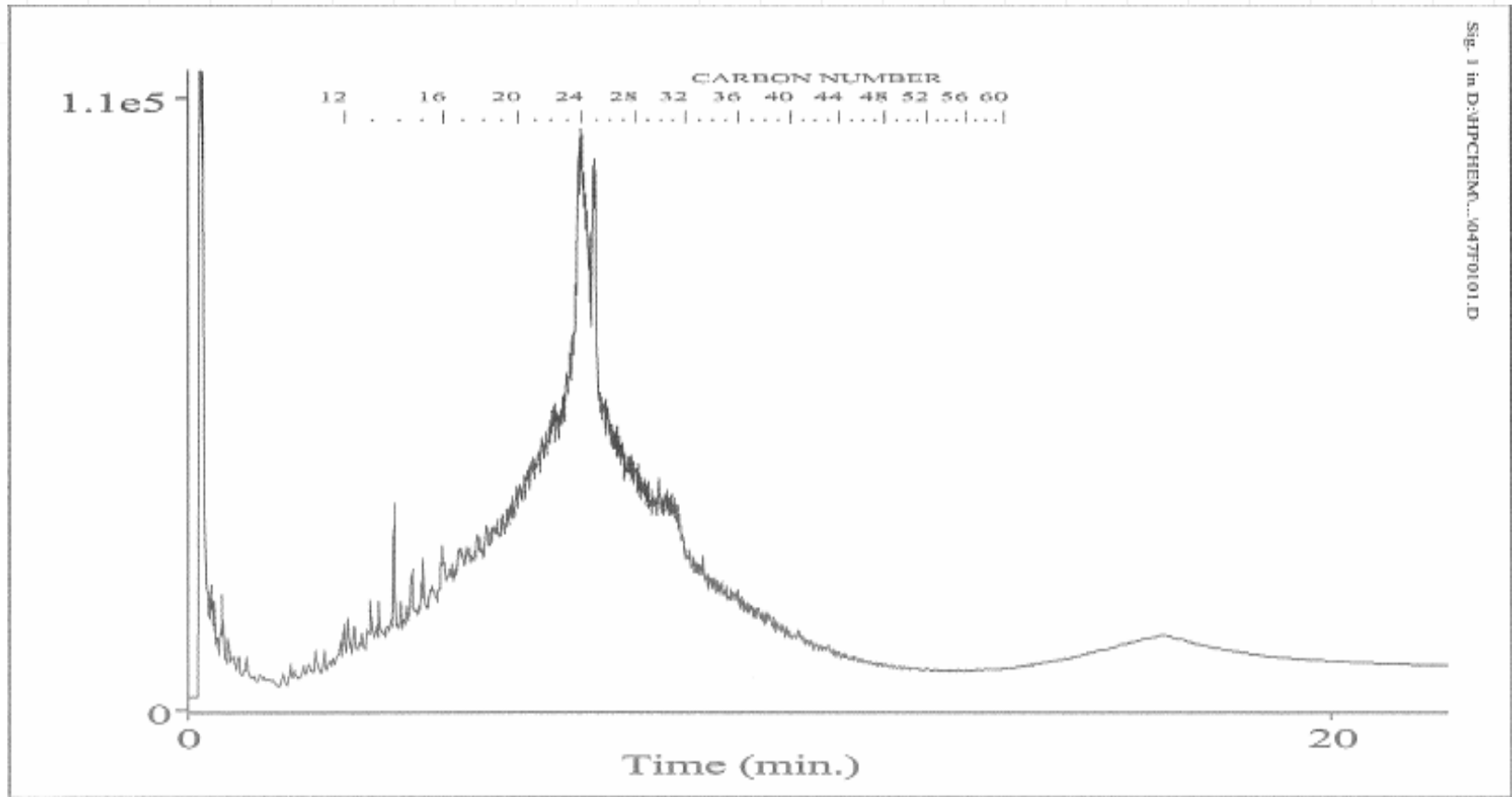


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Coal

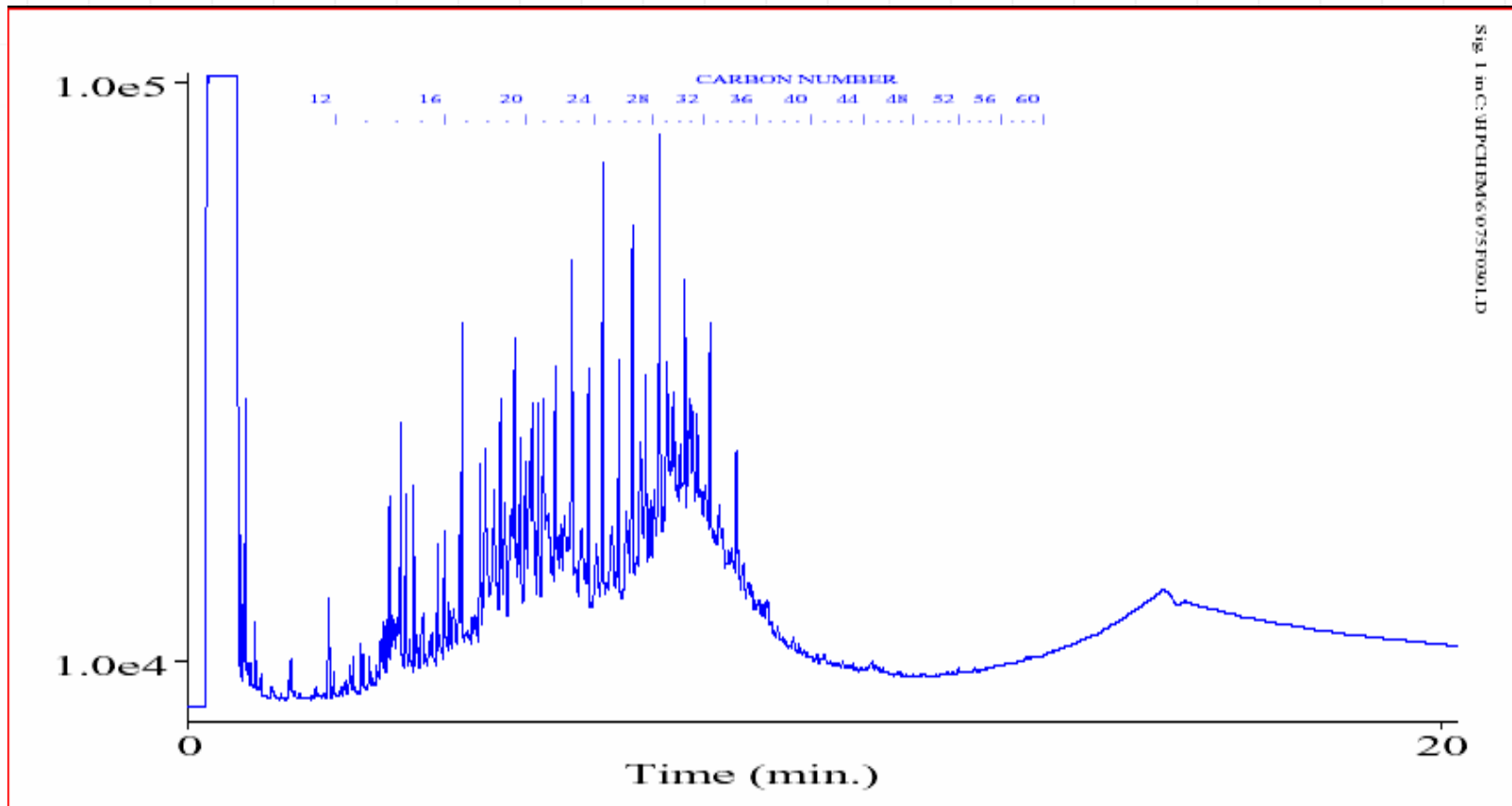
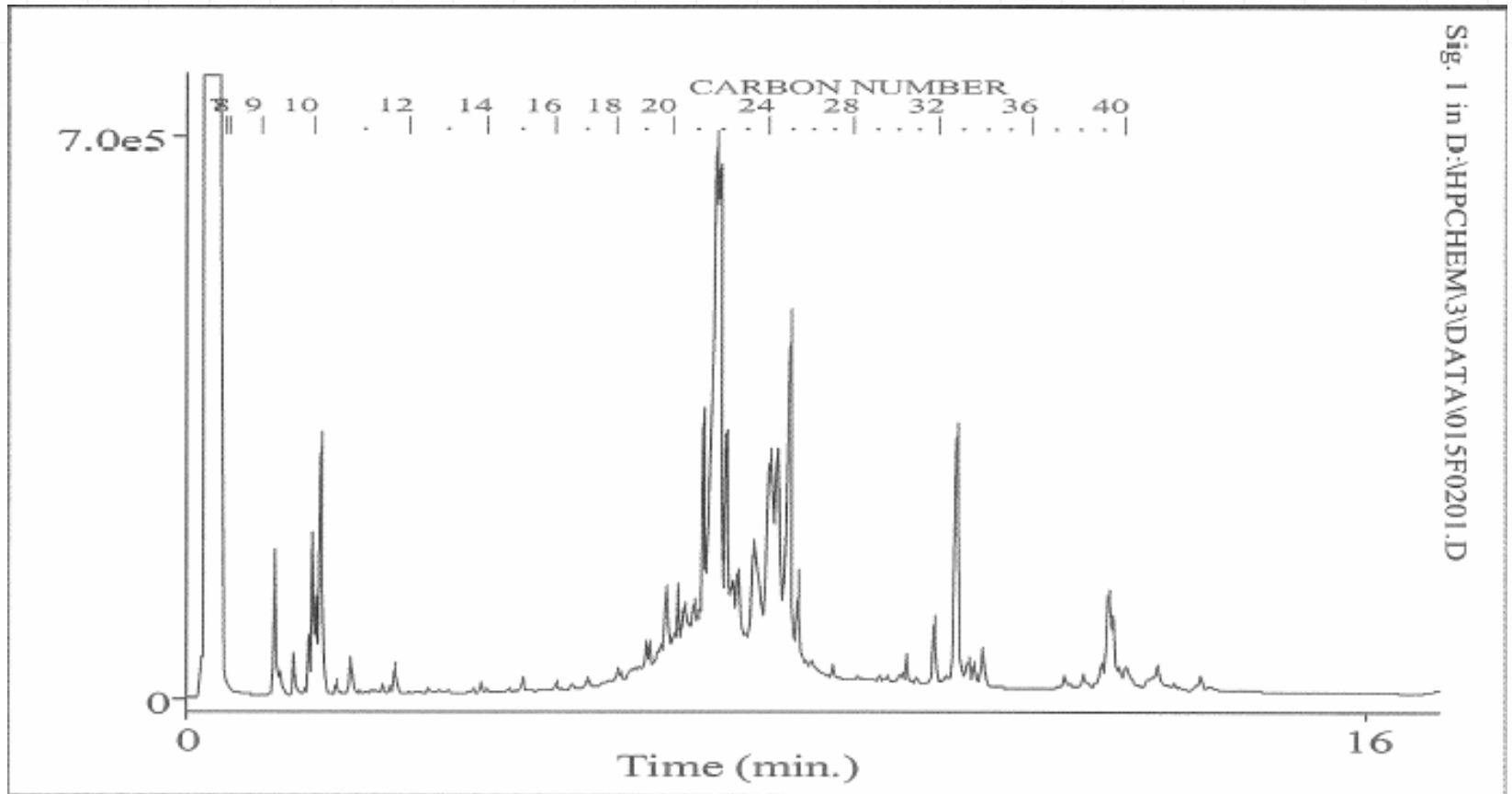


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extracted wood

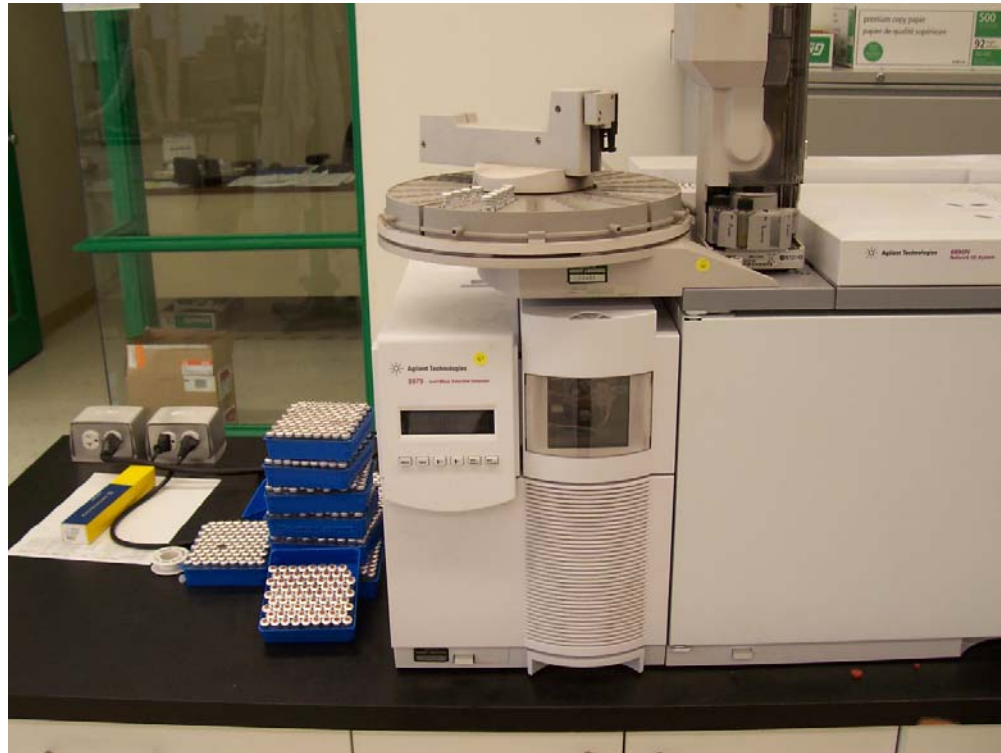


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Example - coal

- $\text{TOC} = \text{TC} - \text{TIC}$ (carbonates)
- $\text{TOC} = ? \text{TOM}$ (LOI)

GC/MS ?



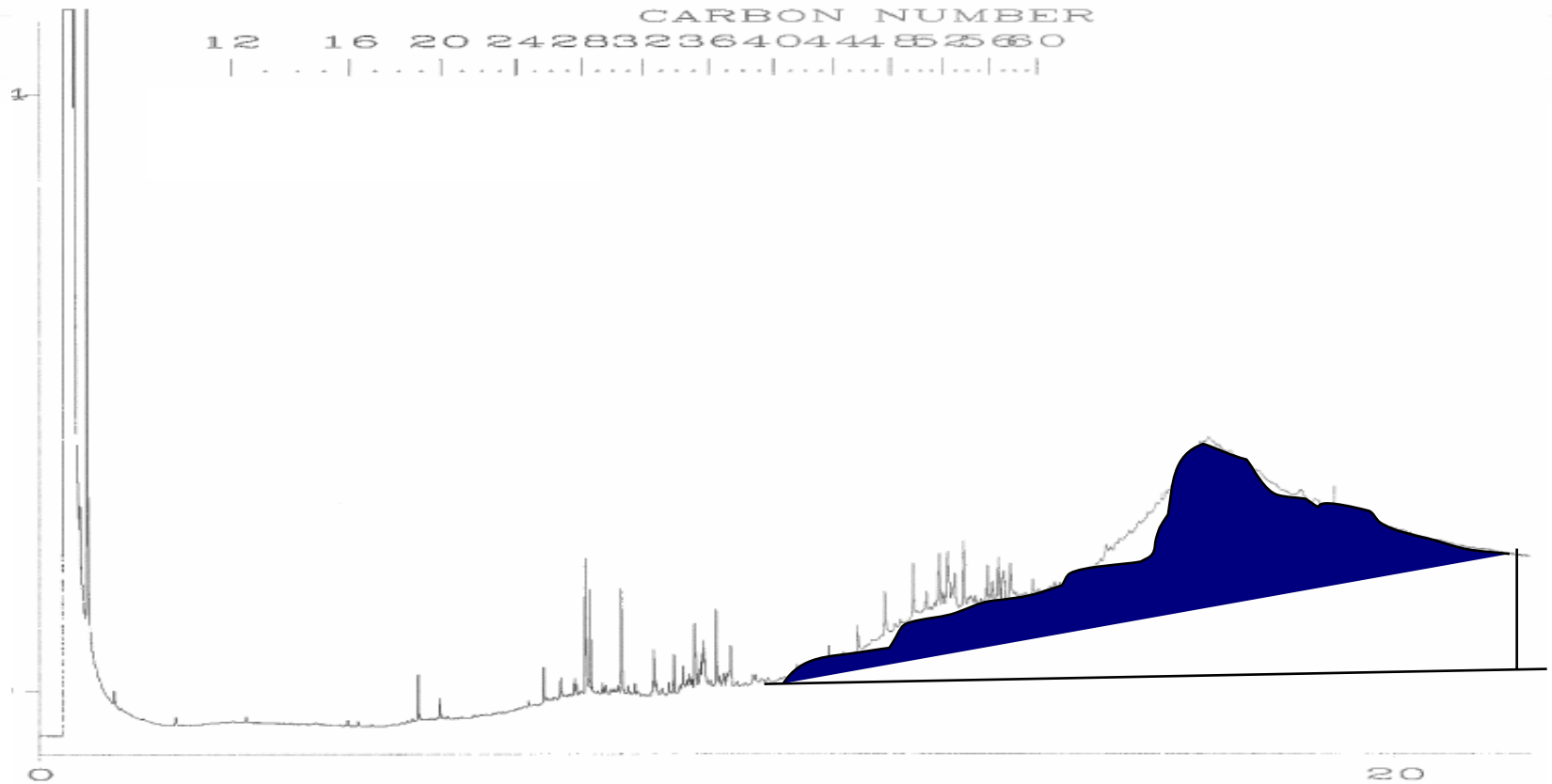
Use of GC/MS

- % plant material – PHC
- Gasoline + plant material
- Ratios
- Still a chromatographic guess.

GC/MS

- Soil + plant material + asphalt
- MOG 2800 mg/kg
- TOC 3.55%
- On GC/MS no PHC detected
- On high temp GC mostly C40+
 - MS would not detect this

Plant material + asphalt



Asphalt + peat

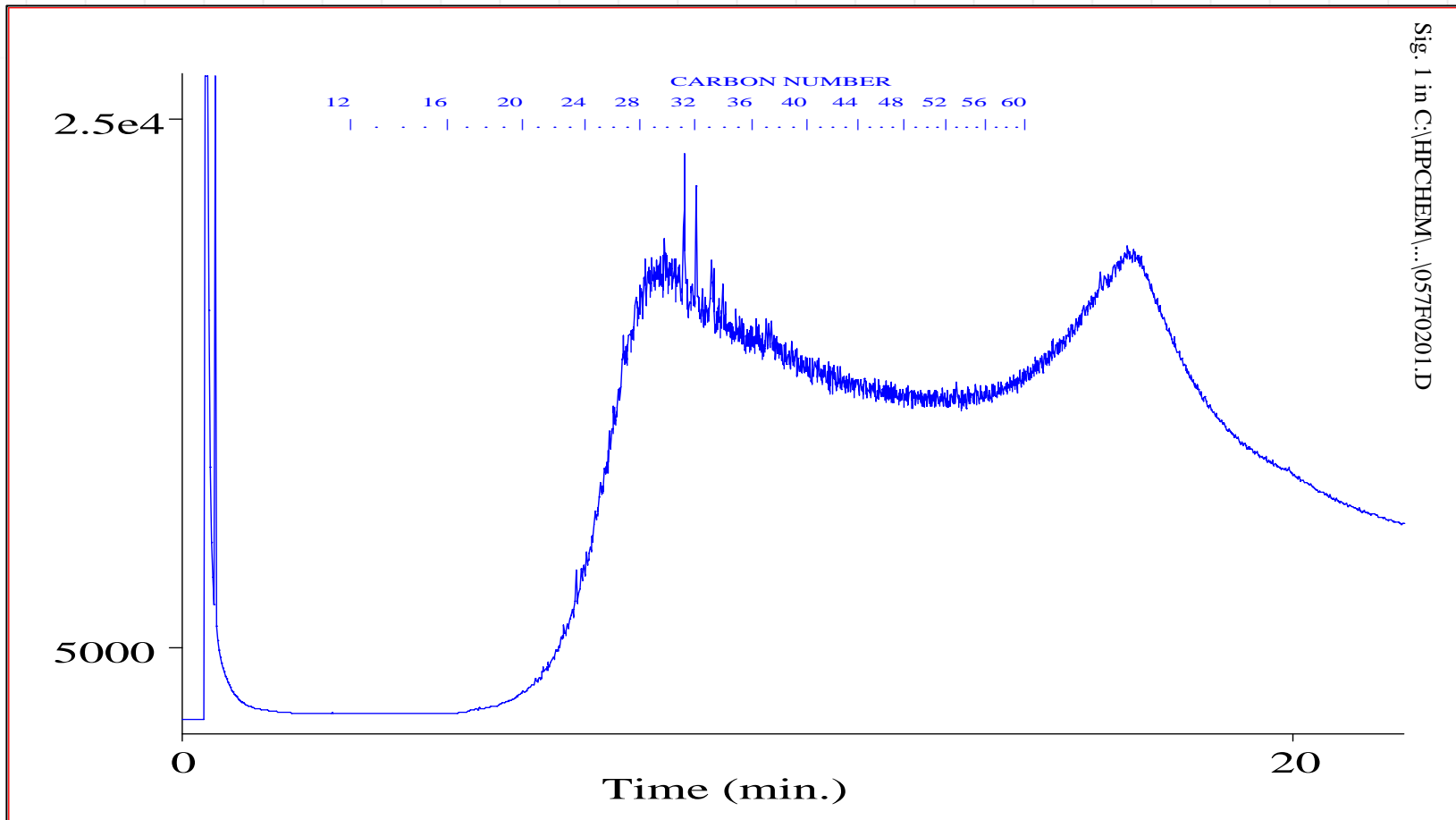
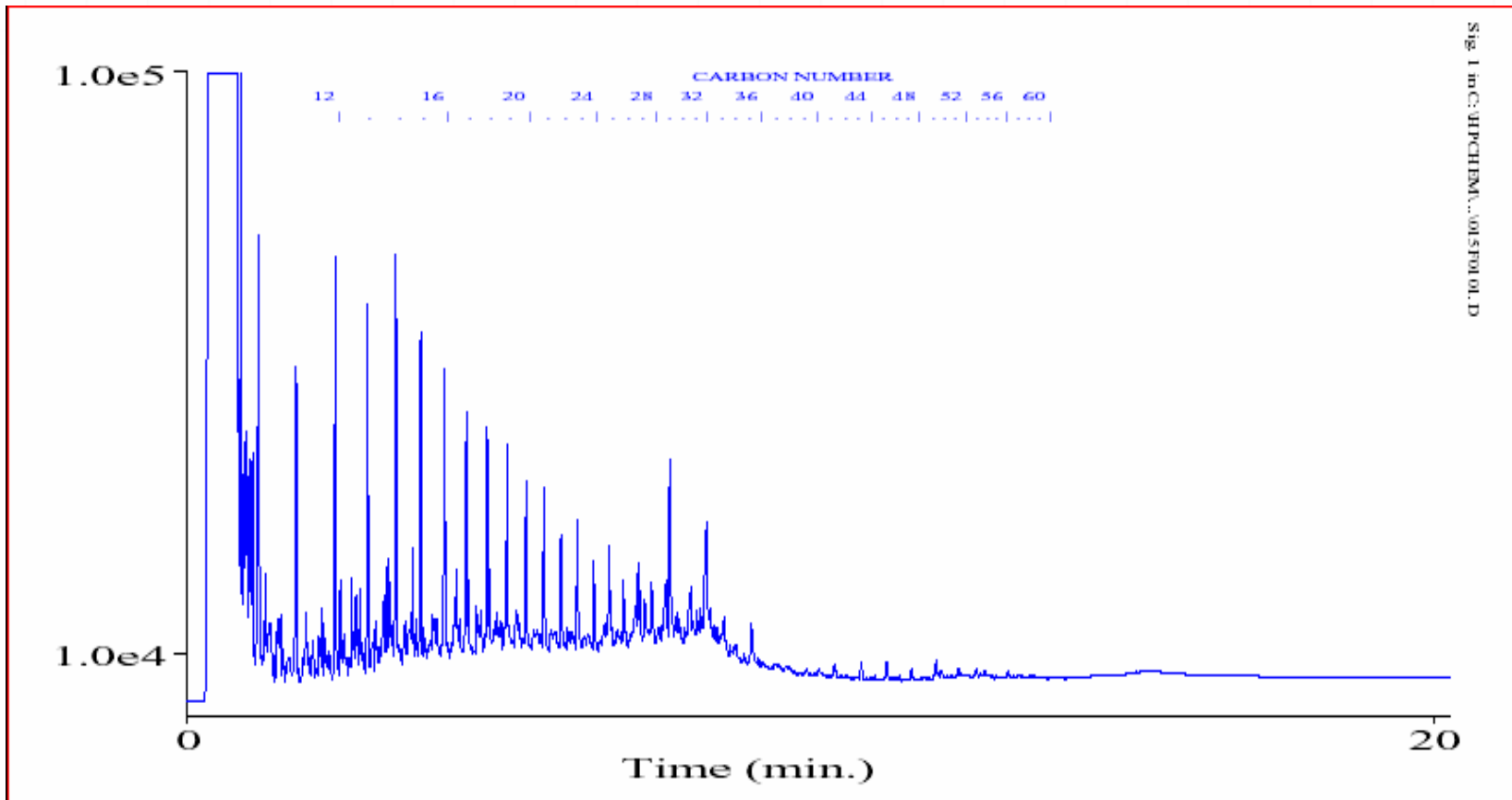


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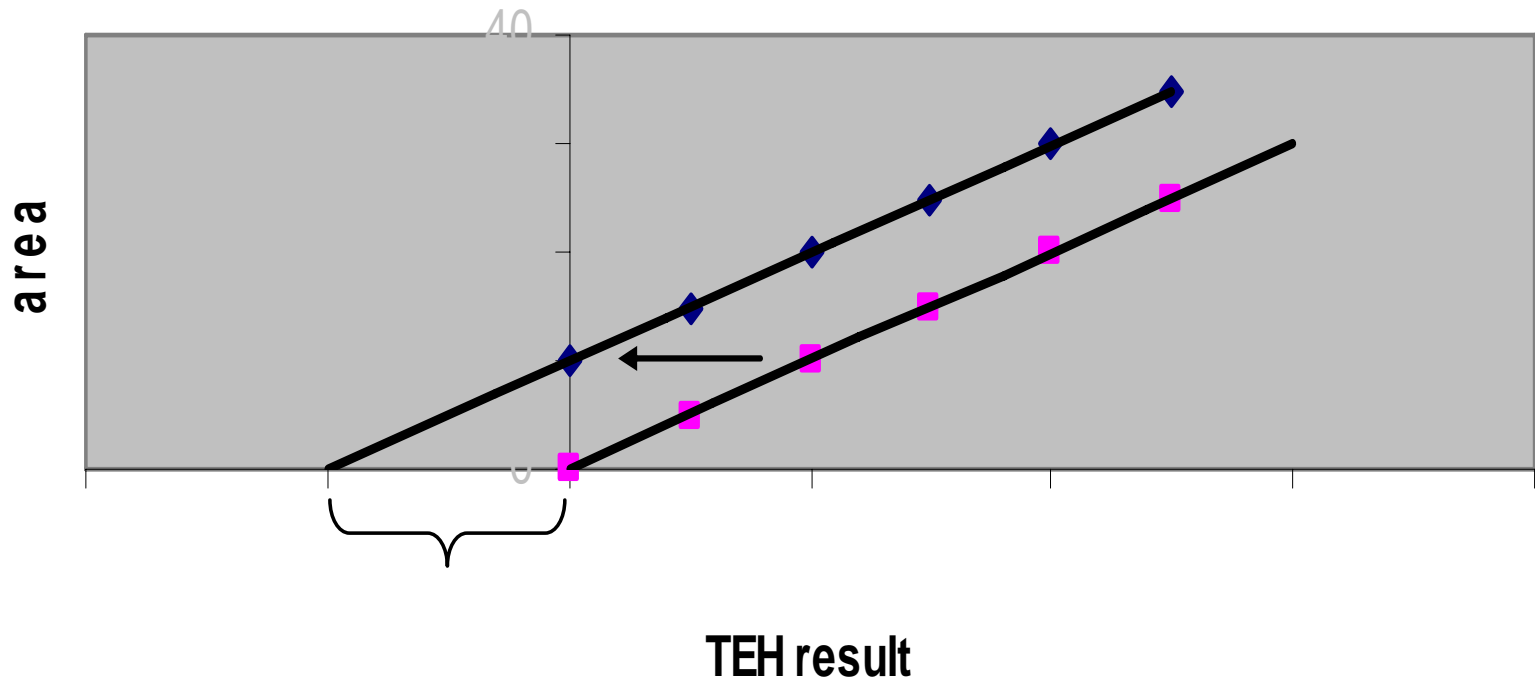
Peat

- Peat + PHC
- no SG done
- Subtract blank peat
- No blank, do extr.HC before and after SG
- 2 silica gel treatments

Fresh crude and peat



standard additions



Standard addition experiments

- Eg % wood by volume
- Works in theory, problem with real samples (normalization)
- TOC before and after extraction
- Bulk density, moisture
- Need relationship between BD and TOC

Combination approach

- Extract sample as per PHC method
- Analyzed for TOC and PHC before and after SG cleanup
- Results used for CTGM interpretation only
 - Presence of biogenic interference
 - Biogenic chromatographic fingerprint
 - Effectiveness of SG cleanup

Some further considerations

- Difference between TOC and LOI
- The need for marker compounds
 - Ratio marker compound/total amendments
- Surrogates for F2 – F4
- Reverse surrogate for SG treatment.