Evaluation of Petroleum Hydrocarbon Methodologies Utilized by the Massachusetts DEP to Assess Potential Exposure in Vapor Intrusion Investigations

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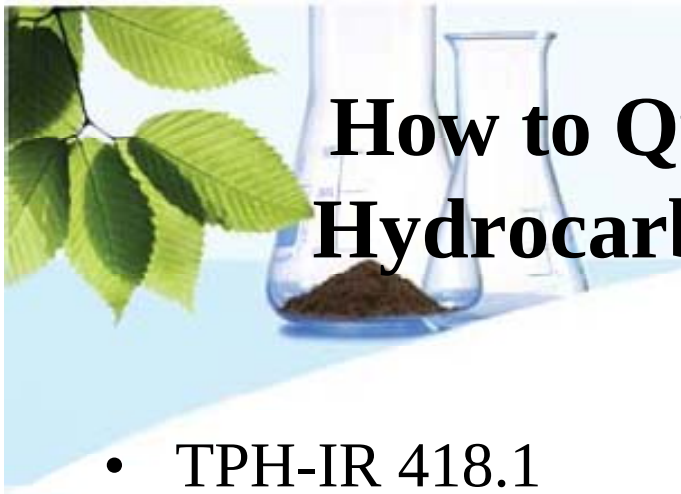

How to Quantitate Petroleum Hydrocarbons-oh let me count thee ways

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- TPH-IR 418.1
- SW-846 mod. 8100 or mod. 8015
- TPH DRO (diesel range organics)
- TPH GRO (gasoline range organics)
- Total Chromatographic Organics (stack testing)

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MADEP –RBCA Approach

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- RBCA approach-(risk based corrective action)
  - incorporate some human health risk based criteria for hydrocarbon classes

- Can separate complex hydrocarbon mixtures into:
  - Collective aliphatic and aromatic **fractions**
  - Distinct hydrocarbon **ranges** within the fractions
  - Individual **target compounds of concern**
    - Can characterizes subsets of hydrocarbons as well as COCs

- Provide necessary data for a toxicological approach to characterize petroleum contaminated media

Petroleum Hydrocarbon and Vapor Intrusion–The MADEP Approach

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- Pathway investigated when groundwater levels are elevated above screening values
- **Volatile** range contamination in soil & GW – VPH method (Volatile Petroleum Hydrocarbons)
- **Semi-volatile** range contamination in soil & GW –EPH method (Extractable Petroleum Hydrocarbons)
- If levels are significant, then the VI risk must be assessed using the APH method (Air-Phase Petroleum Hydrocarbons)

History of Petroleum HC Methodologies in MA

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- EPH & VPH methods
  - First issued in August 1995 by MassDEP,
  - Round Robin conducted-final version issued in 1998
  - Workgroups convened and revisions conducted in 2004 & 2009

MADEP APH History of Method

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- MADEP contracted ENSR's Air Toxics Laboratory to conduct method development in 1999
- Draft method published in December 2000
- MADEP Vapor Intrusion Guidance – April 2002
- Workgroup assembled in December 2008 to finalize method (laboratories, consultants, MADEP staff)
- Final method published in December 2009

MADEP Approach- Petroleum Hydrocarbon Analytical Overview

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- **VPH Method TAL**
  - MTBE, BTEX, Naphthlene, C5-C8 Aliphatics, C9-C12 Aliphatics, C9-C10 Aromatics
- **APH Method TAL**
  - 1,3-Butadiene, MTBE, BTEX, Naphthlene, C5-C8 Aliphatics, C9-C12 Aliphatics, C9-C10 Aromatics
- **EPH Method TAL**
  - Discreet PAHs (17), C9-C18 Aliphatics, C19-C36 Aliphatics, C11-C22 Aromatics

MADEP Approach- Petroleum Hydrocarbon Analytical Overview

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- **VPH Method**
  - Utilizes PID for MTBE, BTEX, Naphthlene, C9-C10 Aromatics. For C5-C8 Aliphatics, C9-C12 Aliphatics, uses FID
- **APH Method**
  - Utilizes MS for all analytes and ranges
- **EPH Method**
  - Uses FID for quantitation of all data. Discreet PAHs & C11-C22 Aromatics are separated by passing extract through silica gel, analyzed separately
- **All Methods specify a specific column!**

MADEP Approach- Petroleum Hydrocarbon Analytical Overview

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- **Hydrocarbon (HC) Range Calibration**
  - All methods (VPH, APH, EPH) use specified alkanes and aromatics to develop a response factor for each calibration level.
  - These alkanes are aromatics are also used for retention time markers to define the range of quantitation for each HC range.
  - The **summation** of the response and concentration for the specified alkanes and aromatics is used in the response factor determination
  - Example:
    - APH C5-C8 Aliphatic HC range uses isopentane, hexane, cyclohexane, 2,3-dimethylpentane, and octane. If the concentration of each compound is 2.0 ug/m^3, then the assigned true value is 10 ug/m^3.

MADEP Approach- Petroleum Hydrocarbon Analytical Overview

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- **VPH/EPH approach being used in…**
  - CT, ME, NJ, NC, MT, PA, WA, IN
- **APH method has also been used in…**
  - MT, WA, ME, and soon CT

APH Method – Detailed Review

Method requirements

QA/QC

Technical challenges

Data interpretation

MADEP APH –Why is it better for petroleum contaminated sites?

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- TO-15 poor at quantitating petroleum-related compounds and the cummulative health risk associated with HCs

	MINERAL SPIRITS	#2 FUEL OIL	GASOLINE	KEROSENE
TO-15 SUM OF HITS, ug/m^3	1,488,000	974,900	638,000	261,900
APH SUM OF HITS, ug/m^3	21,983,000	6,469,000	4,300,000	4,082,000
APH/TO-15 Ratio	14.8	6.6	6.7	15.6

APH Method Specifications- System Requirements

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- Specified column = Rtx-1 (or similar phase, i.e. DB-1)
- Tune criteria for BFB spectrum same as TO-15
- No MDL study required, use lowest calibration point for RL
- Uses MS as detector
- Concentrator must have moisture and CO_2 controls
- Only gaseous phase standards allowed

APH Method Specifications- Initial Calibration Criteria

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- Linear range 1.0 ug/m^3 ~ 500 ug/m^3 (HC ranges are greater)
- Minimum of 5 points for initial calibration
- 30% maximum RSD (naphthalene max. = 40%)
- Injection volumes of calibration standards must be the same range as that used for samples
  - If “1X” volume is 250 mL, and minimum volume used for dilutions is 25 mL, then same range of volume must be used during initial calibration

Hydrocarbons used to Quantitate Ranges

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Compound	Used for Quantitation of Hydrocarbon Range…
Isopentane	C_5-C_8 Aliphatic
Hexane	
cyclohexane	
2,3-dimethylpentane	
n-heptane	
n-octane	
2,3-dimethylheptane	C_9-C_{12} Aliphatic
n-nonane	
n-decane	
Butylcyclohexane	
n-undecane	
n-dodecane	
Isopropylbenzene	C_9-C_{10} Aromatic
1-methyl-3-ethylbenzene	
1,3,5-trimethylbenzene	
p-isopropyltoluene	
1,2,3-trimethylbenzene	

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MADEP APH –Mass Spectrometer vs. FID Comparison

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- MS typically not used for petroleum quantitation, usually an FID utilized

	MINERAL SPIRITS	#2 FUEL OIL	GASOLINE	KEROSENE
C5-C8 Aliphatics, FID	523	6241	9211	686
C5-C8 Aliphatics, MS	664	6709	7789	802
%D	-23.8	-7.2	16.7	-15.5
C9-C12 Aliphatics FID	2422	4066	160	1894
C5-C8 Aliphatics, MS	3099	4496	241	2816
%D	-24.5	-10.0	-40.6	-39.1

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QA/QC Comparison to TO-15

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Method	TO-15	APH
Units	ppbV and ug/m^3	ug/m^3
QA / QC	Dup, blank, CC/LCS	Dup, blank, CC, LCS
LCS Recovery Limits	70-130%	70-130% (Naph 40%)
Duplicate %D Limits	25%	30%
LCS/Tune Check Frequency	Every 24-hr or 20 samples	Every 24-hr or 20 samples
Internal Standard Recovery Limits	60-140%	50-200%

APH Method Specifications- Data Reduction Challenges

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- Aliphatic Ranges use total ion response
- Aromatic range uses summation of ions 120 and 134 over retention time range
- All targets and ranges use internal standard quantitation (extrapolated ion response for internal standard)
- Internal standard and surrogate(s) (if used) response must be subtracted from corresponding aliphatic range
- Discreet target analyte concentration must be subtracted from corresponding range
- Aromatic range must be subtracted from C9-C12 Aliphatic range

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Use of Mass Spectrometer in APH- Advantage

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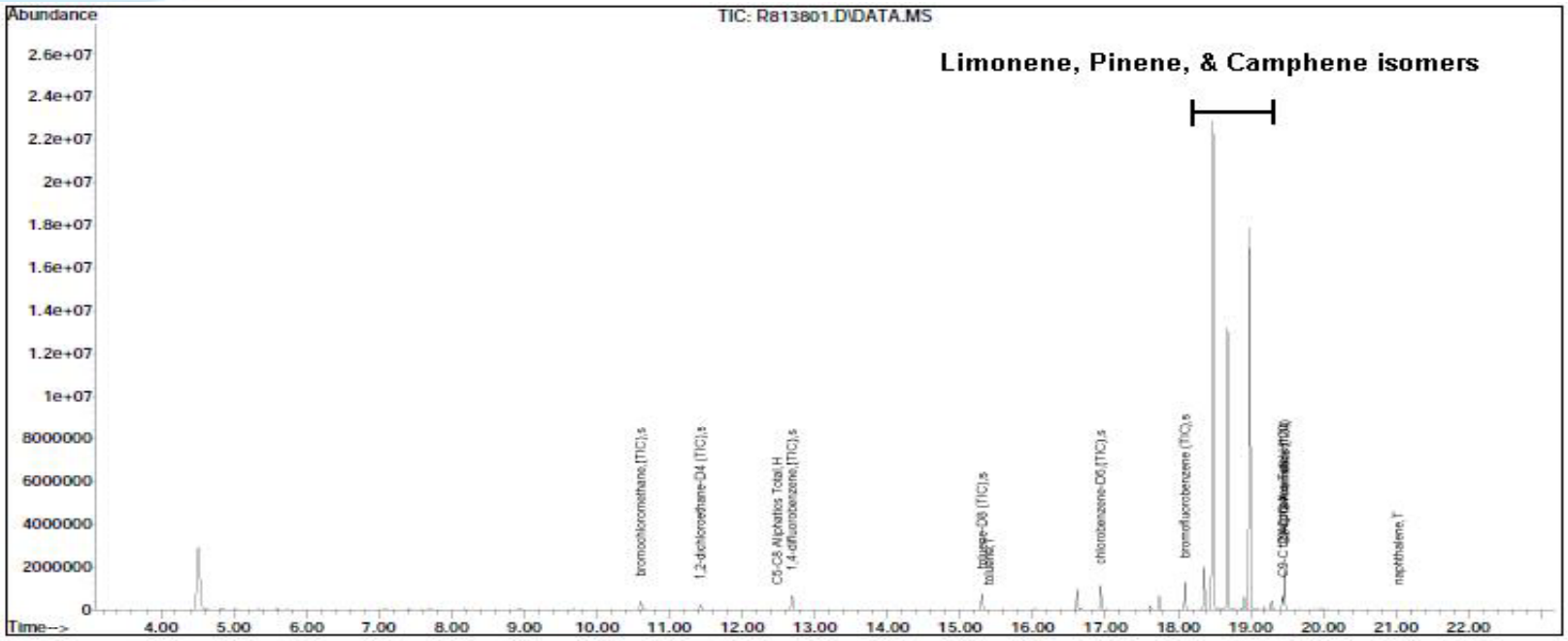

"Data user" has the option to subtract out "non-petroleum hydrocarbons" if suspected

Use of Mass Spectrometer in APH- Advantage

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- Previous chromatogram - Results changed from 41,000 ug/m^3 to “ND” for C9-C12 Aliphatic range
- Other common non-petroleum HC in the C5-C8 Aliphatic range: Acetone, MEK, THF, TCE, PCE, siloxane isomers
- If ranges are adjusted, lab must narrate what is subtracted

Reporting Requirements for the APH Method

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- Lab reporting requirements
  - Sample results
  - Method Blank
  - LCS
  - Matrix duplicate
  - Internal standard performance
  - Media certification results
  - Flow controller calibration results
  - Vacuum of canister at receipt in lab (should be less than -4 in. Hg delta field vs. lab)

Sampling with the APH Method

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- Specifies the use of canisters – passivated (SUMMA, or fused silica-lined)
- Canisters must be batch-certified
- Tedlar bags not accepted
- Does not specify sampling protocols in method, i.e. flowrates, durations, etc.
- No field QC required in method (i.e. field duplicates, trip blanks)
- Can be adopted to sampling protocols in state-specific VI guidance

Ambient Air Sampling Evaluation of Field Duplicate Samples

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	Indoor Air Sampling						Outside		
Compound	sample	sample field dup	RPD	sample	sample field dup	RPD	sample	sample field dup	RPD
Methyl tert butyl ether	12.0	12.6	5.1	5.7	5.8	1.2	ND	ND	NA
Benzene	2.6	2.4	6.3	2.1	2.1	2.4	ND	ND	NA
Toluene	11.2	11.8	5.2	7.7	8.0	4.2	ND	ND	NA
Ethylbenzene	2.1	2.1	1.0	1.5	1.5	1.3	ND	ND	NA
m/p-Xylenes	6.7	6.7	0.9	5.3	5.4	1.1	ND	ND	NA
o-Xylene	2.9	2.8	0.7	2.2	2.2	0.9	ND	ND	NA
Naphthalene	2.0	1.9	0.5	1.9	2.3	18.8	ND	ND	NA
C5-C8 Aliphatics, Adjusted	87.0	87.5	0.5	73.1	74.6	2.1	19.2	30.5	45.7
C9-C12 Aliphatics, Adjuste	104.8	105.1	0.3	114.6	126.0	9.4	21.6	17.3	22.0
C9-C10 Aromatics	21.6	21.4	1.0	21.0	21.2	1.1	ND	ND	NA

Background Associated with the APH Target Analytes

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- Problem assessing APH data from indoor air….
- Elevated levels of petroleum HCs typically found in indoors
- Fortunately, background study conducted in MA by Haley & Aldrich and Alpha Analytical was done for APH parameters

COMPOUND	Frequency of Detection	Minimum Detected Concentration	Maximum Detected Concentration	Median Conc.	75TH %ILE	90TH %ILE
1,3-Butadiene	1 /100	1.10	1.10	0.87	1.10	1.10
TOLUENE	90 / 100	1.99	944	7.62	17.9	42.5
C5-C8 ALIPHATICS	83 / 100	24.9	1,240	58	125	329
C9-C12 ALIPHATICS	80 / 100	30	3,270	68.3	110	222
M/P-XYLENE	45 / 100	2.54	81.9	2.99	7.41	20.5

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APH Background
Possible Sources

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Aromatic Compounds	Sources
Benzene (30%)	Degreaser, adhesive remover
Toluene (95%)	Auto parts cleaner, PVC cement, Rust Oleum and Krylon spray paint
Xylenes (95%)	Parts cleaner, spray paint, flea foggers, wallboard adhesive
Naphthalene	Moth balls, gas treatment, animal repellant

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APH Ranges
Typical Indoor Air
Background Data

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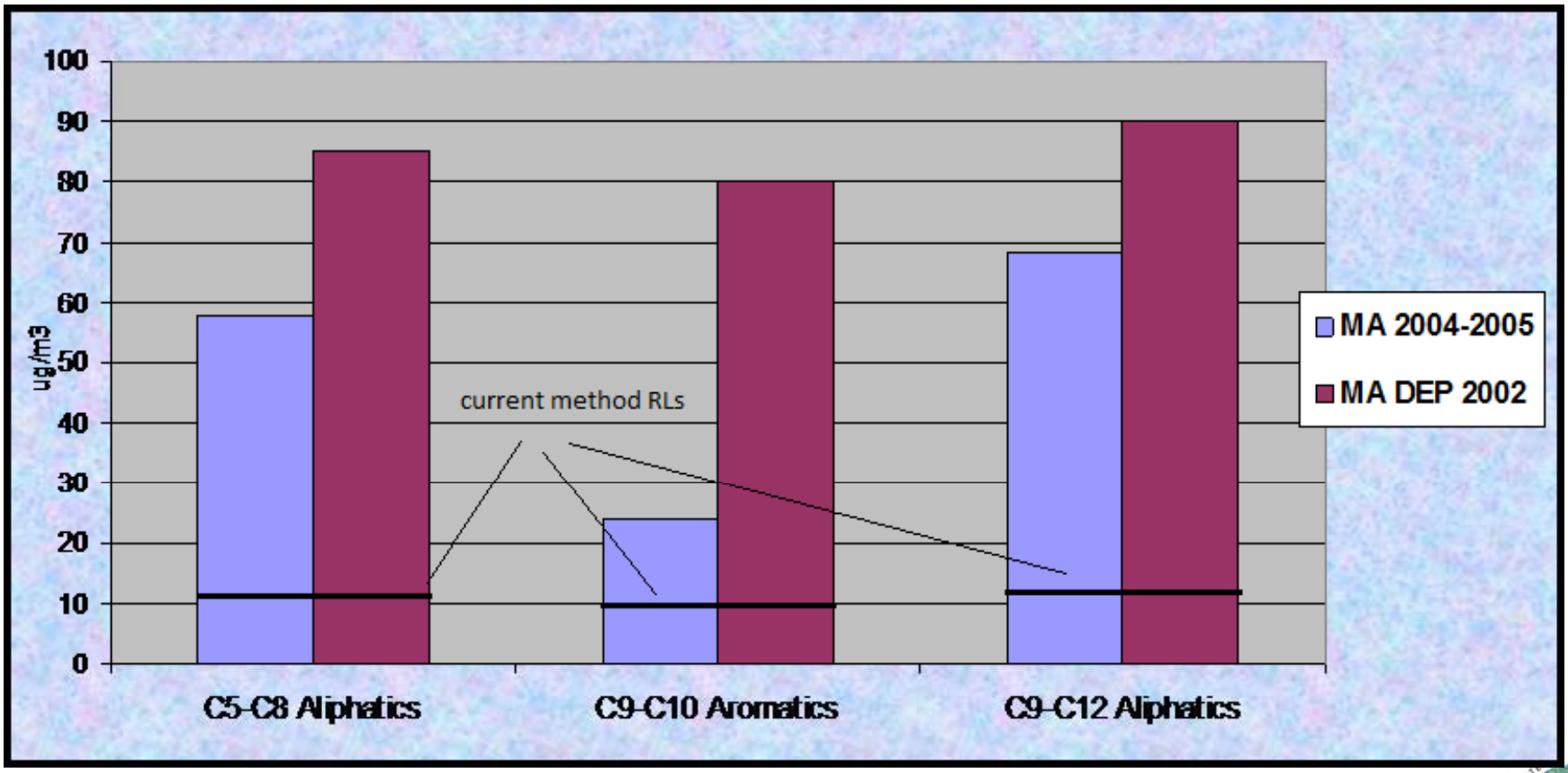

Aliphatic and Aromatic Hydrocarbon Contributors to Background

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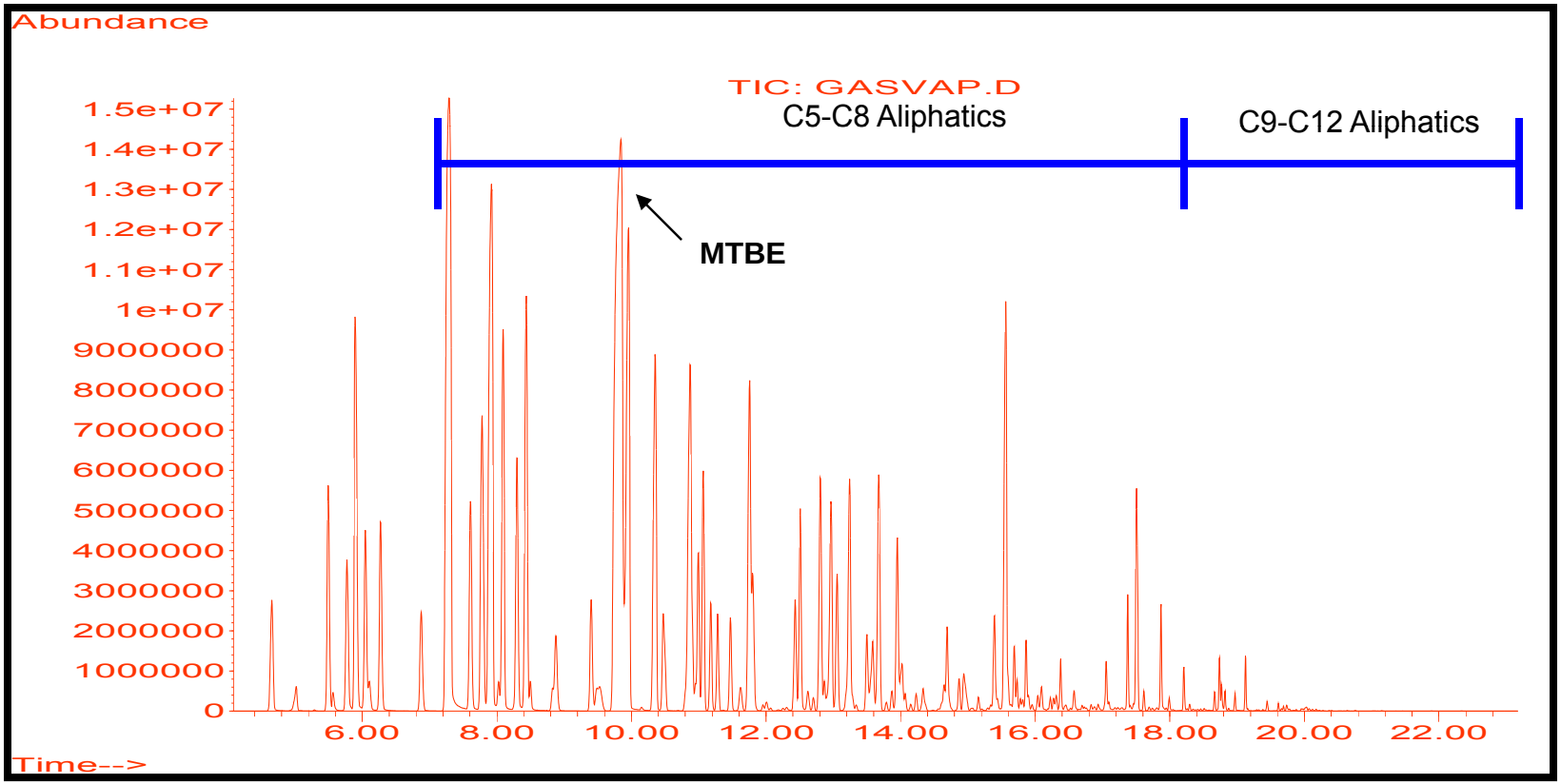
Gasoline Vapor Phase

RR=71



Aliphatic and Aromatic Hydrocarbon Contributors to Background

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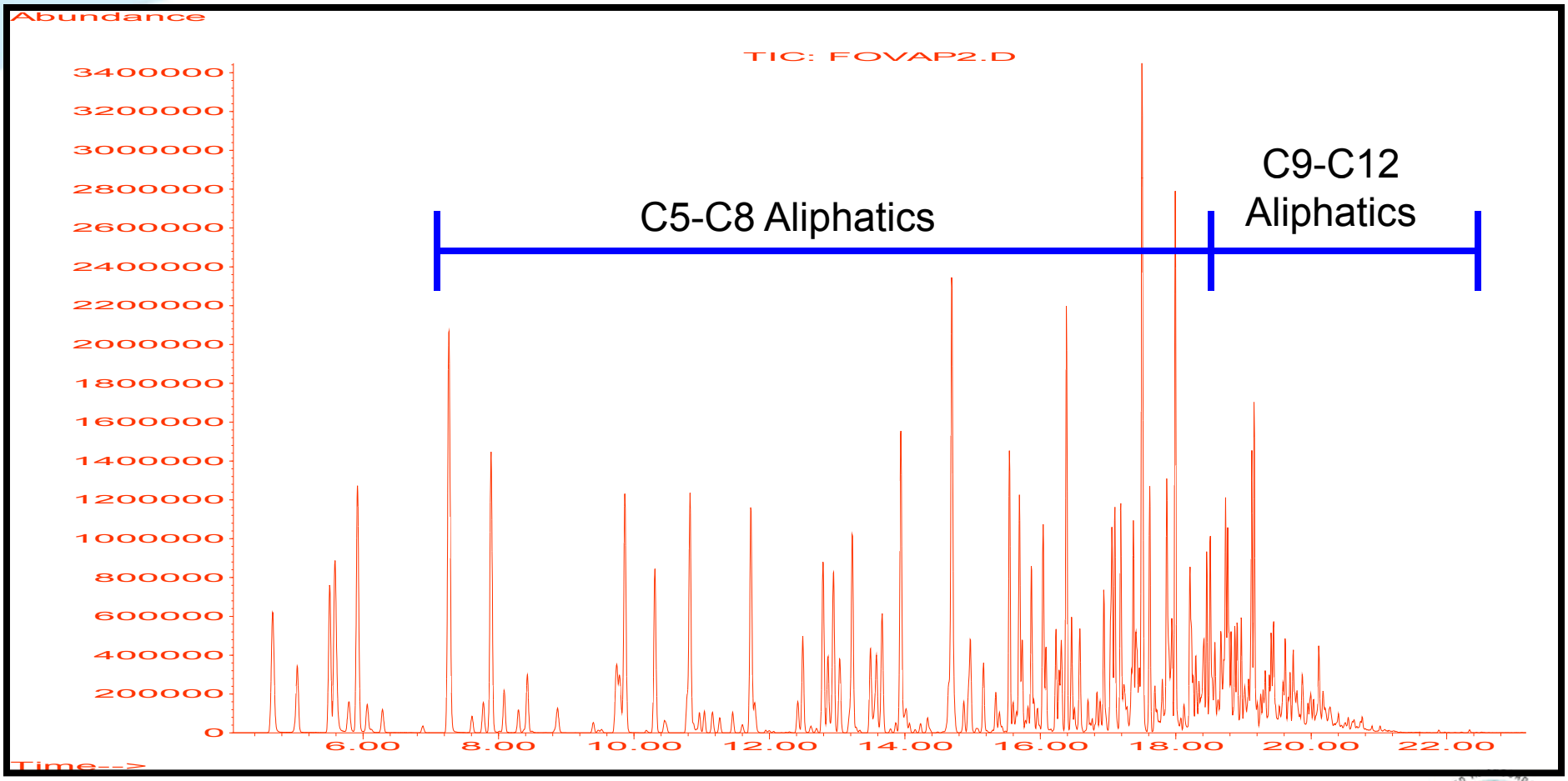
#2 Fuel Oil Vapor Phase
RR=7



Aliphatic and Aromatic Hydrocarbon Contributors to Background

Oil Based Paint Vapor Phase

RR=1.3

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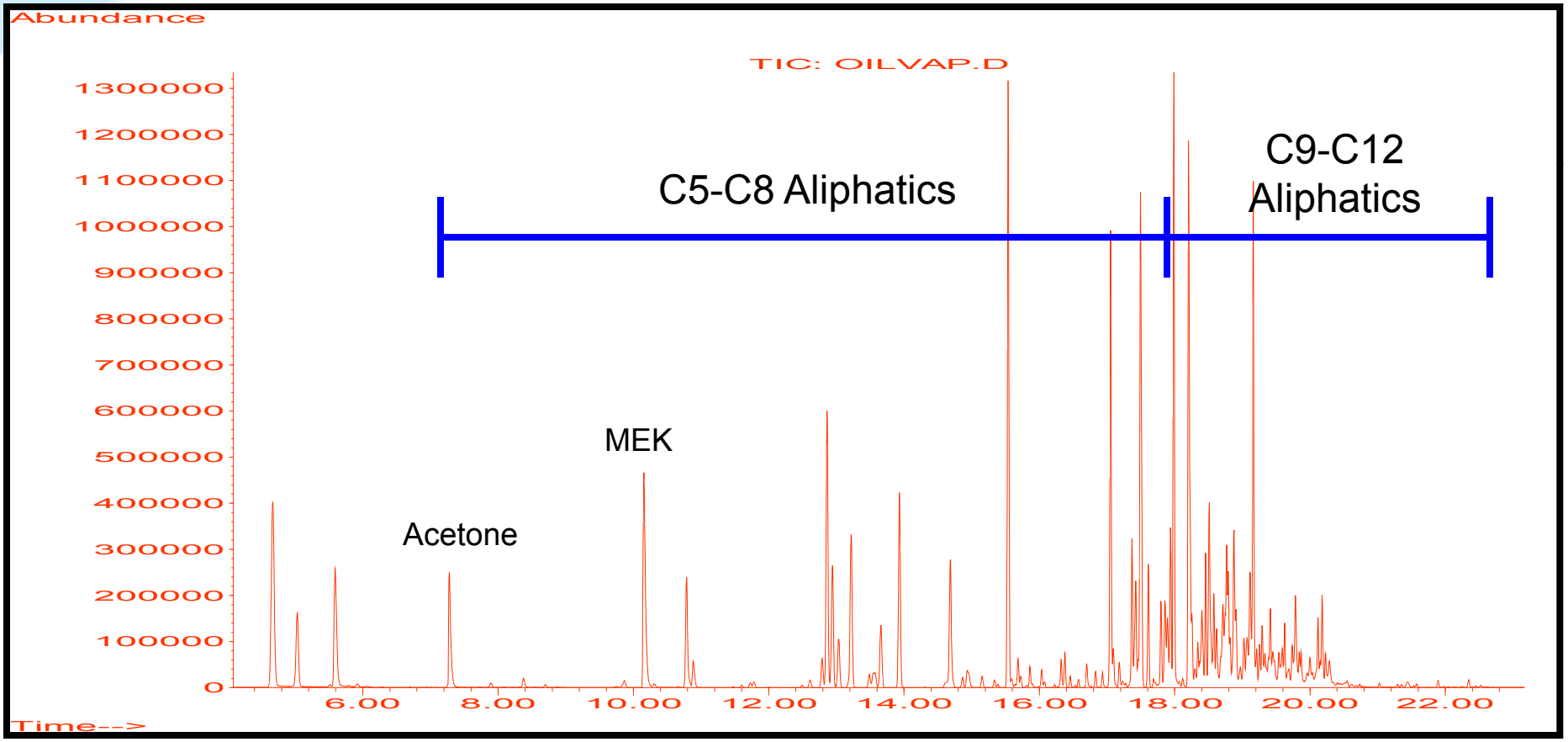

Aliphatic and Aromatic Hydrocarbon Contributors to Background

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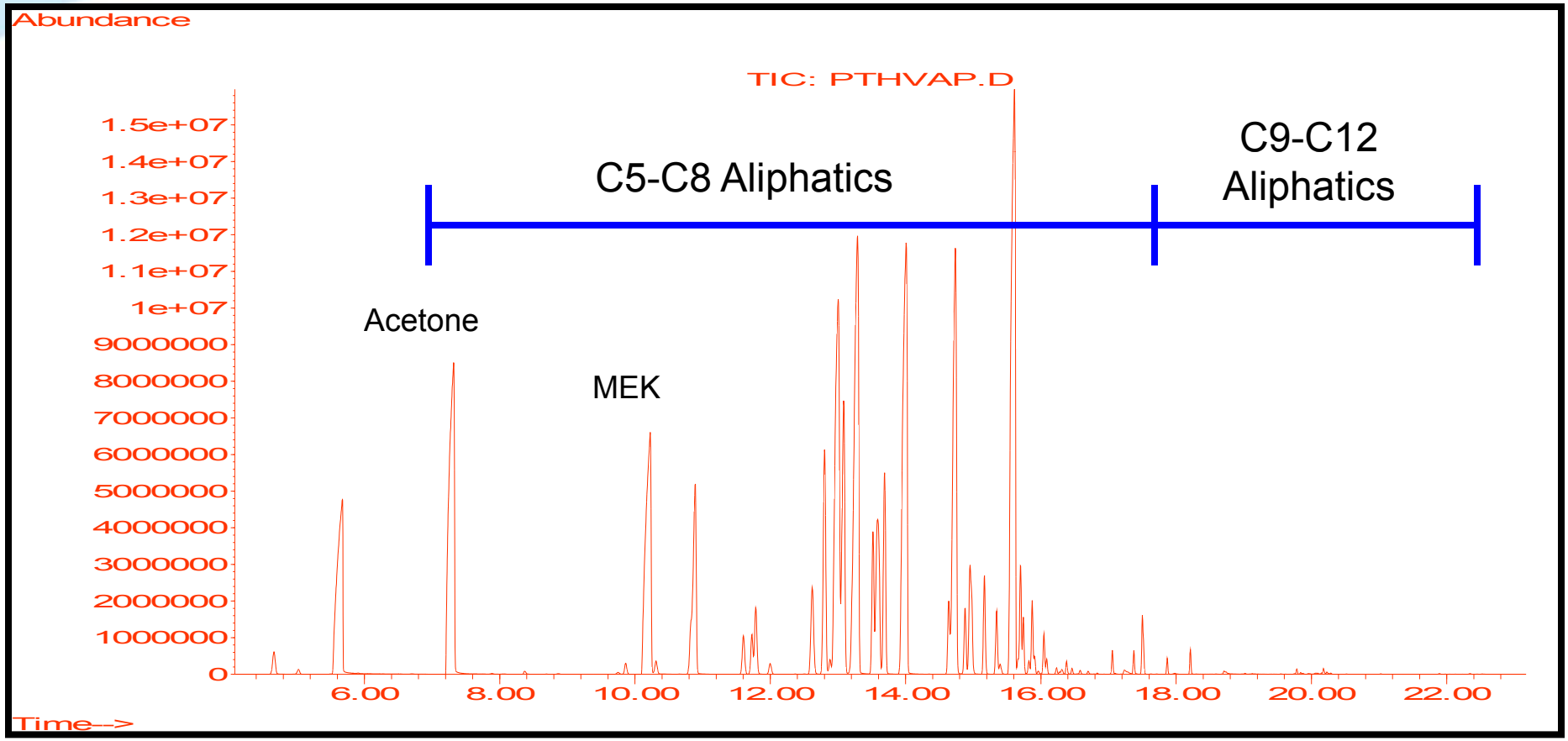
Paint Thinner Vapor Phase
RR=213



Aliphatic and Aromatic Hydrocarbon Contributors to Background

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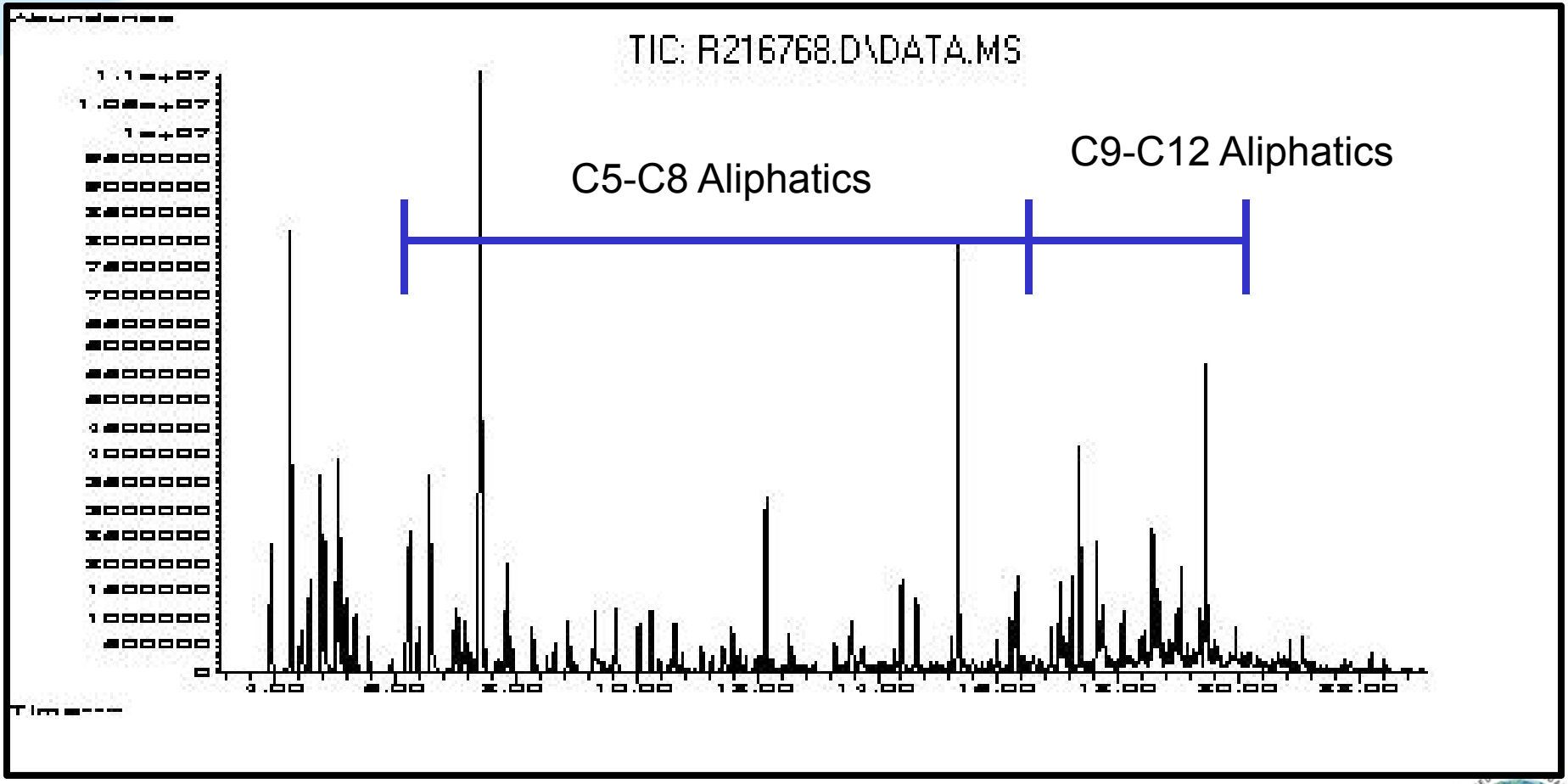
Second Hand Smoke (aka Nancy's lungs)



Advantages / Disadvantages of APH Method

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Advantage

- Captures more of the petroleum contamination than standard TO-15
- Can utilize same equipment as used for TO-15
- Use of MS allows for removal of non-petroleum hydrocarbons causing positive bias

Disadvantage

- Most quantitation software not sophisticated enough to perform data reduction calculations. Need to download to spreadsheet or modify software.
- Gaseous phase standard additional cost

Review

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- History of petroleum HC methodology
- MADEP TPH Approach
- Detailed Review of APH Method requirements
- Potential Background Sources

Questions ?

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Thank you for your attention