



Application of an Analytical Technique for Determining Alkyl PAHs, Saturated Hydrocarbons and Geochemical Biomarkers

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PAHs and Alkyl PAHs

- Most important target analytes in damage assessment from petroleum products
- Known to originate from 2 sources
 - Petrogenic
 - Pyrogenic

PAHs and Alkyl PAHs

- Can be used in forensic analysis to qualitatively fingerprint petroleum sample
 - Crude oils contain primarily alkyl PAHs and relatively smaller concentrations of unsubstituted PAHs
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What are Alkyl PAHs?

- Parent PAHs are 2 or more fused conjugated rings
 - naphthalene
 - chrysene
- Alkylated PAHs are the parent PAH with various alkyl groups attached
 - 2,3,5-trimethylnaphthalene
 - 7,12-dimethylchrysene

What are Alkyl PAHs?

- Categorized by the total number of alkyl carbon atoms present
 - A homolog group includes all of the isomers with the same number of carbon atoms
 - C3 includes propyl, isopropyl, trimethyl and ethylmethyl
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What are Alkyl PAHs?

- Parent PAHs that are isomers of other parent PAHs are combined for reporting purposes
 - phenanthrene/anthracene
 - fluoranthene/pyrene
 - benz(a)anthracene/chrysene

Why do we care?

- Traditional methods focused on the 16 Priority Pollutant PAHs identified by EPA
 - There are hundreds if not thousands of alkylated forms that are unaccounted for in traditional methods
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Why do we care?

- Less toxicity data available for alkyl PAHs than their parent compounds
 - Alkyl PAHs are more abundant and persist longer than their parent compounds
 - Analysis of alkyl PAHs in combination with the parent compounds is a better estimation of total exposure to toxic effects of PAHs
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Method Summary

- Extraction methods are relatively standard for those used for soil and water
 - SW-846 3510 for waters
 - SW-846 3546 for soils
 - Alumina column clean-up used as needed
 - GPC and/or Silica gel for tissue samples
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Method Summary

- Tuning and calibration similar to 8270 SIM
 - Alkyl PAHs calculated from a multipoint calibration
 - A representative target compound is used to represent a homolog series for quantification
 - Results generated for alkyl PAHs should be treated as semiquantitative
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PAHS Reported

Acenaphthene

Acenaphthylene

Anthracene

Benzo(a)anthracene

Benzo(a)pyrene

Benzo(b)fluoranthene

Benzo(e)pyrene

Benzo(g,h,i)perylene

Benzo(k)fluoranthene

Benzothiophene

Biphenyl

Chrysene

cis/trans-Decalin

Dibenz(a,h)anthracene

Dibenzofuran

Dibenzothiophene

Fluoranthene

Fluorene

Indeno(1,2,3-cd)pyrene

Naphthalene

1-Methylnaphthalene

2-Methylnaphthalene

2,6-Dimethylnaphthalene

2,3,5-Trimethylnaphthalene

Naphthobenzothiophene

Perylene

Phenanthrene

1-Methylphenanthrene

Pyrene

Retene

Alkyl PAHS Reported

C1-Naphthalenes

C2-Naphthalenes

C3-Naphthalenes

C4-Naphthalenes

C1-Fluorenes

C2-Fluorenes

C3-Fluorenes

C1-Phenanthrenes/Anthracenes

C2-Phenanthrenes/Anthracenes

C3-Phenanthrenes/Anthracenes

C4-Phenanthrenes/Anthracenes

C1-Benzo(b)thiophene

C2-Benzo(b)thiophene

C3-Benzo(b)thiophene

C4-Benzo(b)thiophene

C1-Naphthobenzothiophenes

C2-Naphthobenzothiophenes

C3-Naphthobenzothiophenes

C1-Decalin

C2-Decalin

C3-Decalin

C4-Decalin

C1-Dibenzothiophenes

C2-Dibenzothiophenes

C3-Dibenzothiophenes

C4-Dibenzothiophenes

C1-Fluoranthenes/pyrenes

C2-Fluoranthenes/pyrenes

C3-Fluoranthenes/pyrenes

C4-Fluoranthenes/pyrenes

C1-Benzanthrene/chrysenes

C2-Benzanthrene/chrysenes

C3-Benzanthrene/chrysenes

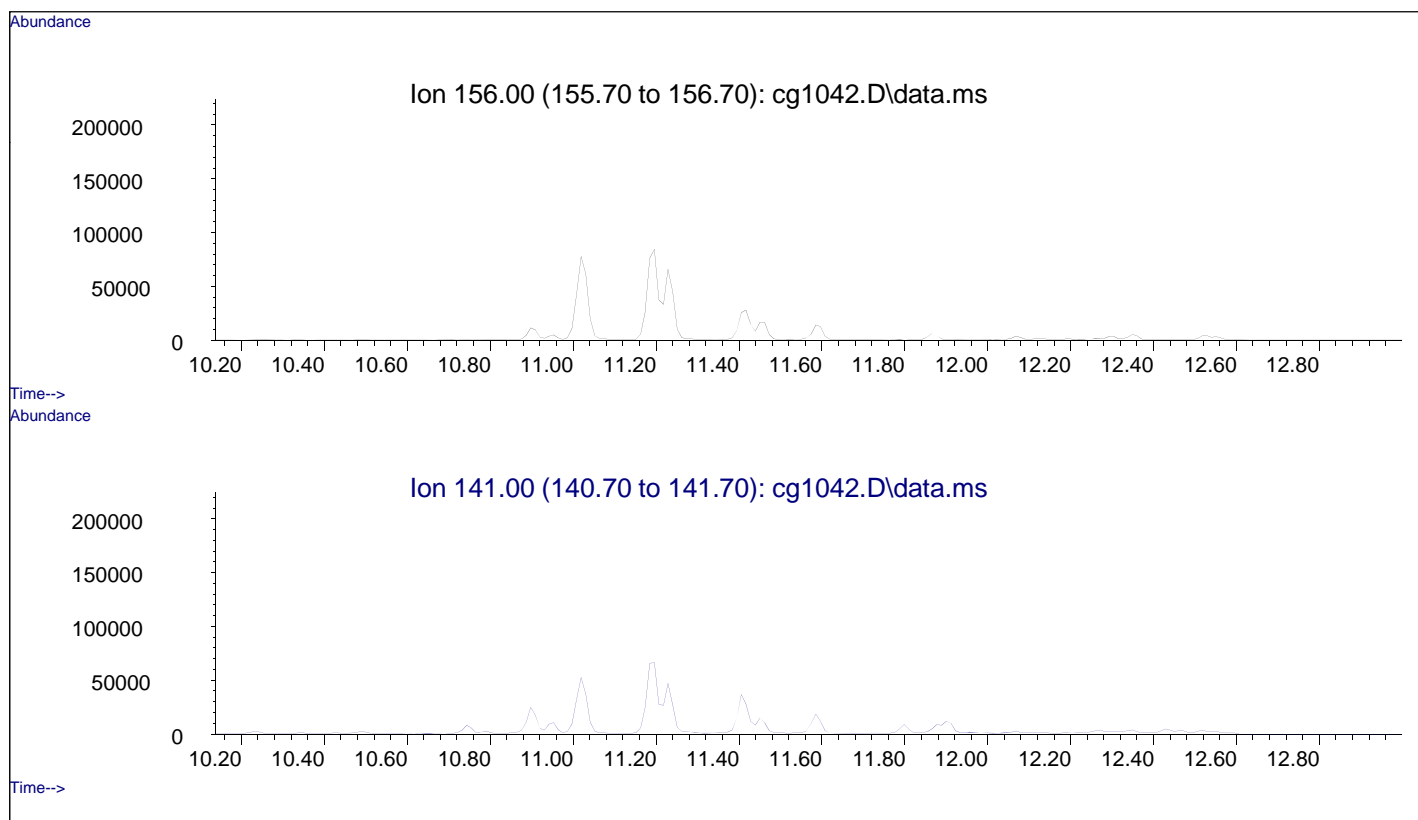
C4-Benzanthrene/chrysenes

Method Summary

- To create SIM method large investment in establishing correct windows
 - Analysis of reference oils to determine alkyl PAH windows
 - Requires analysis of windowing standard at start of each tune
 - Alkanes added to the calibration and analysis mix
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C2-Naphthalenes

Mass 156, 141 amu; 10.2 to 12.8 min



Alkanes Reported

n-Decane

n-Undecane

n-Dodecane

n-Tridecane

n-Tetradecane

n-Pentadecane

n-Hexadecane

n-Heptadecane

n-Octadecane

n-Nonadecane

n-Eicosane

n-Heneicosane

n-Docosane

n-Tricosane

n-Tetracosane

n-Pentacosane

n-Hexacosane

n-Heptacosane

n-Octacosane

n-Nonacosane

n-Triacontane

n-Hentriacontane

n-Dotriacontane

n-Tritriacontane

n-Tetratriacontane

n-Pentatriacontane

Pristane

Phytane

What are Geochemical Biomarkers?

- Complex organic compounds that are found in petroleum and show little to no change in structure from their parent molecules found in living organisms.
- Categorized into different classes, terpanes, steranes and triaromatic steroids

What are Geochemical Biomarkers?

- Several reference biomarker compounds are in calibration mixes
 - Biomarkers grouped according to reference used for quantification
 - Analysis of reference oils key to biomarker identification
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Biomarkers reported

A1-C20-TAS	T4-C23Diterpane	T20-Moretane	S4-Diacholestane
A2-C21-TAS	T9-C29Tricyclitriterpane(S)	T21-C31-Homohopane(S)	S5-Diacholestane
A3-C26 TAS(20S)	T10-C29Tricyclitriterpane(R)	T22-C31-Homohopane(R)	S14-Cholestane(20R)
A4-C26/C27-TAS	T11-Trisnorhopane(TS)	T22a-Gammacerane	S15-Cholestane(20S)
A5-C27-TAS(20R)	T12-Trisnorhopane(TM)	T26-C32-Bishomohopane(S)	S22-Methylcholestane(20R)
A6-TAS(20S)	T13-Trisnorhopane	T27-C32-Bishomohopane(R)	S23-Methylcholestane(20S)
A7-TAS(20R)	T13a-29,30-Bisnorhopane	T30-C33-Trishomohopane(S)	S24-Methylcholestane
	T15-C29-Norhopane	T31-C33-Trishomohopane(R)	S25-Ethylcholestane
	T16-Norneohopane	T32-Tetrakishomohopane(S)	S26-Ethylcholestane(20R)
	17a(H)-diahopane	T33-Tetrakishomohopane(R)	S27-Ethylcholestane(20S)
	T17-C30-Normoretane	T34-Pentakishomohopane(S)	S28-Ethylcholestane
	T18-C30-Oleanane	T35-Pentakishomohopane(R)	
	T19-C30-Hopane		

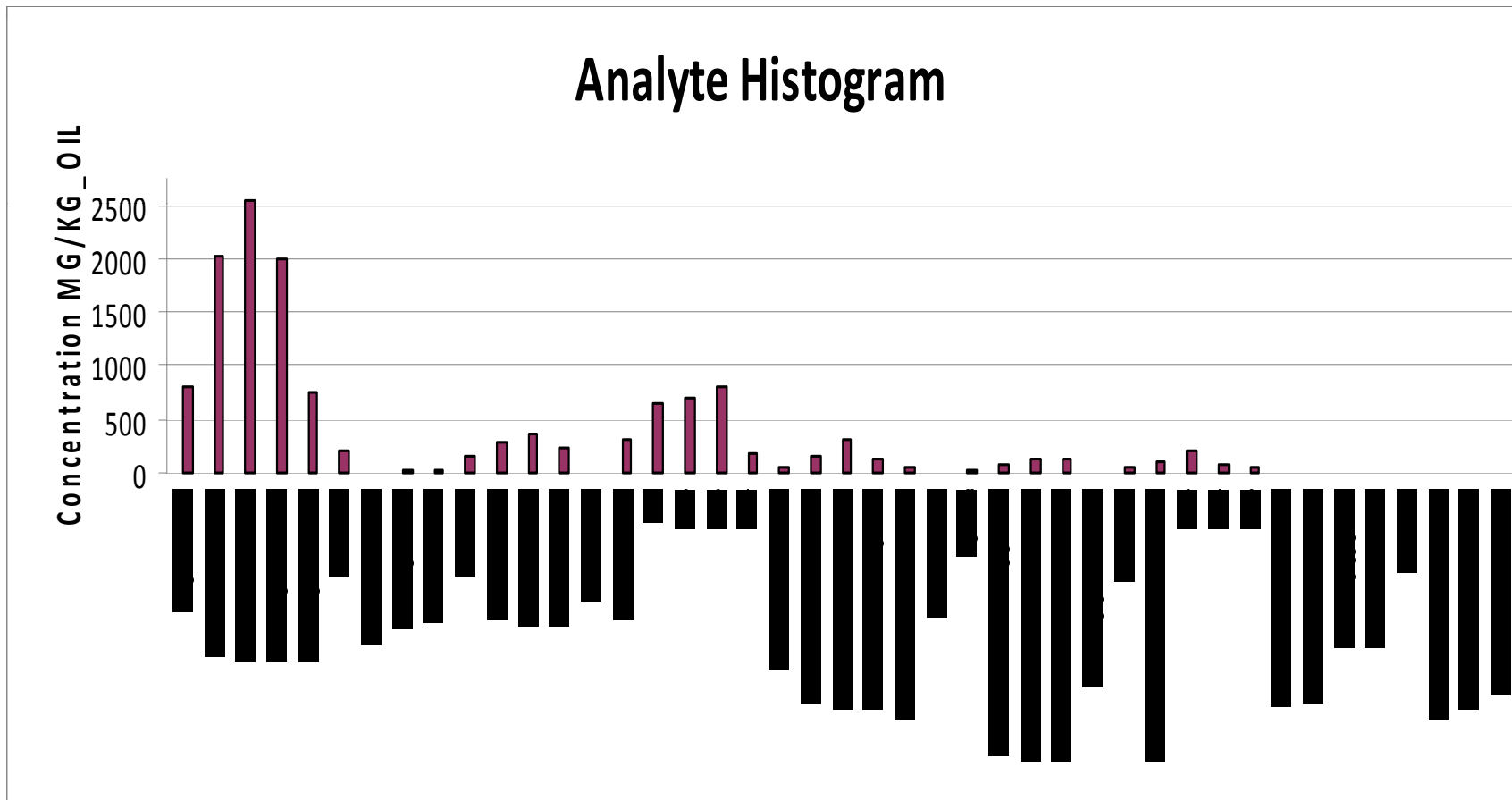
Why do we care?

- Very useful in forensic petroleum analysis when alkane pattern is weathered
 - Complements and enhances conventional GC/FID fingerprinting capabilities
 - Can be analyzed simultaneously with the Alkyl PAHs.
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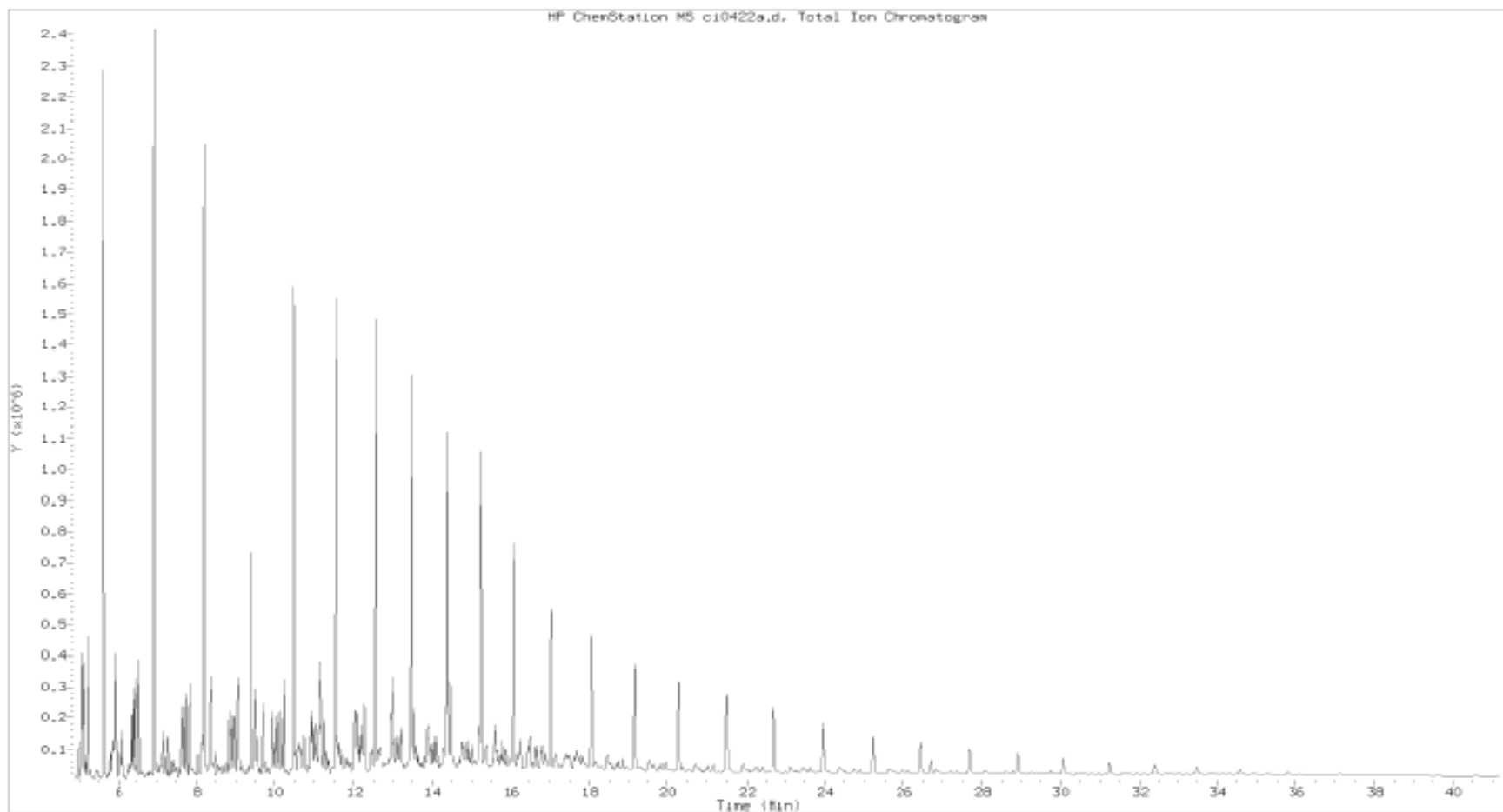
Results

- Specialized report format and electronic spreadsheet
 - Histograms for qualitative analysis of PAHs/Alkyl PAHs
 - Extracted ion current profiles provided for biomarkers
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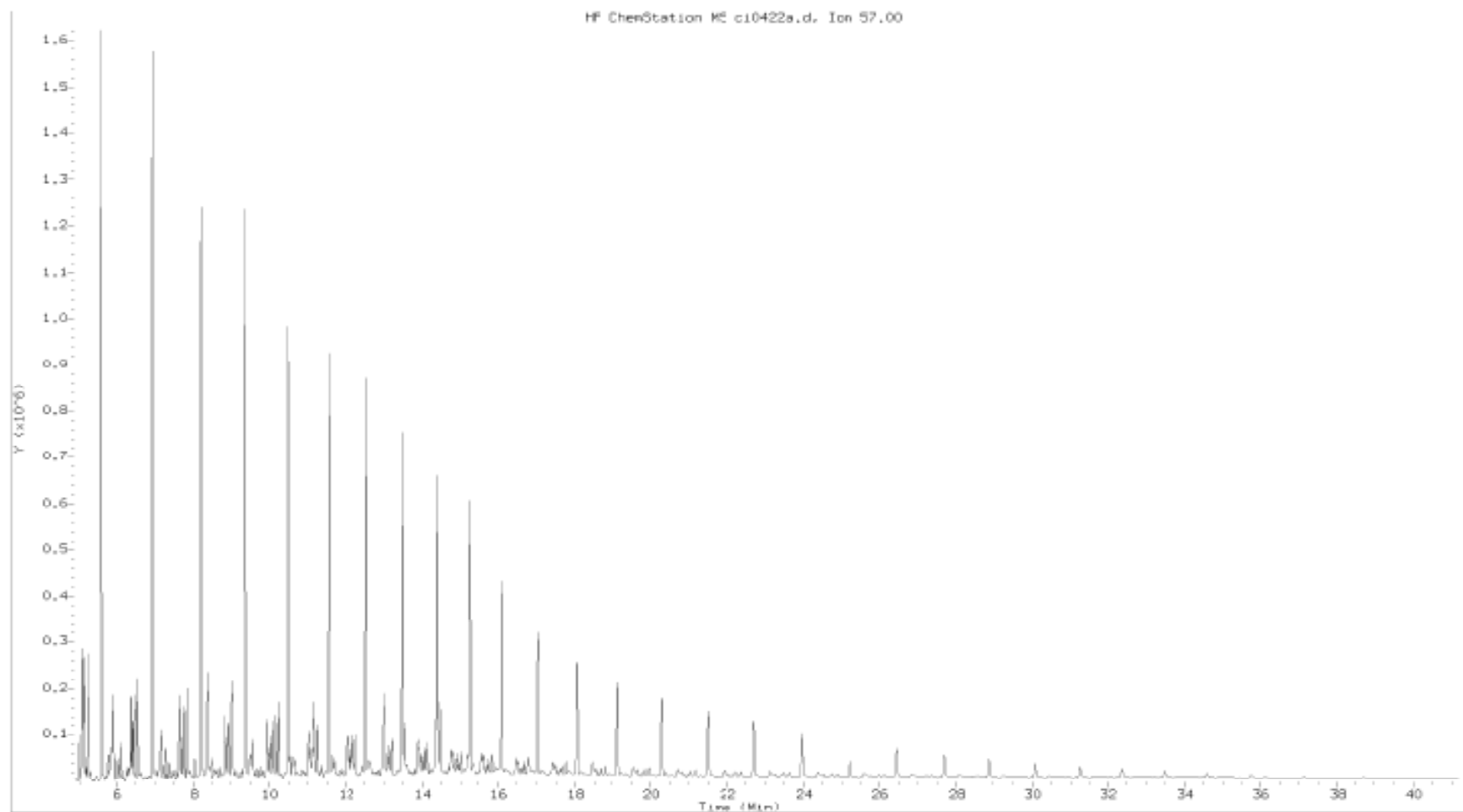
PAH/Alkyl PAH Histogram



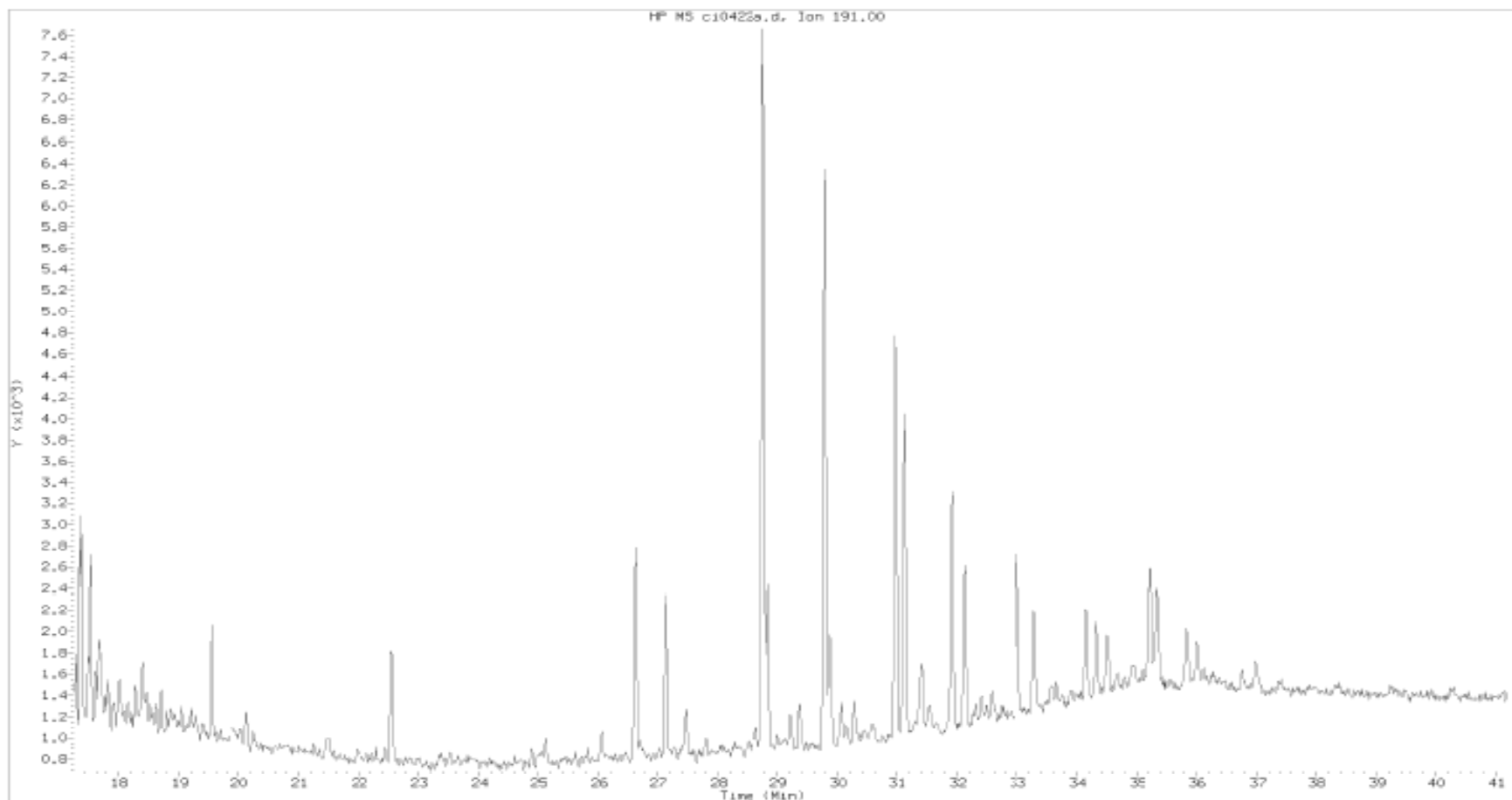
Arabian Light – Total Ion Chromatogram



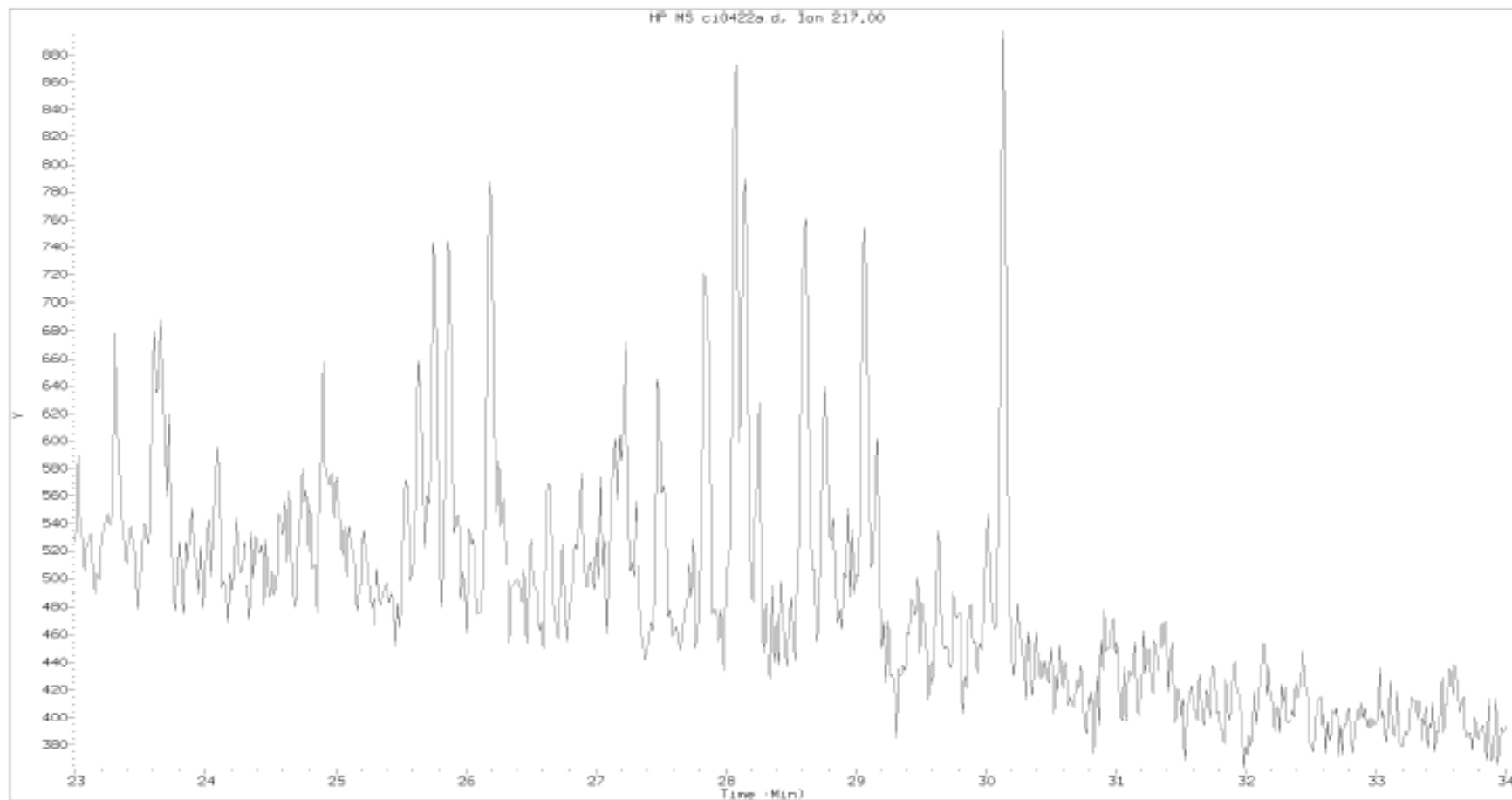
Arabian Light – Mass 57 amu EICP



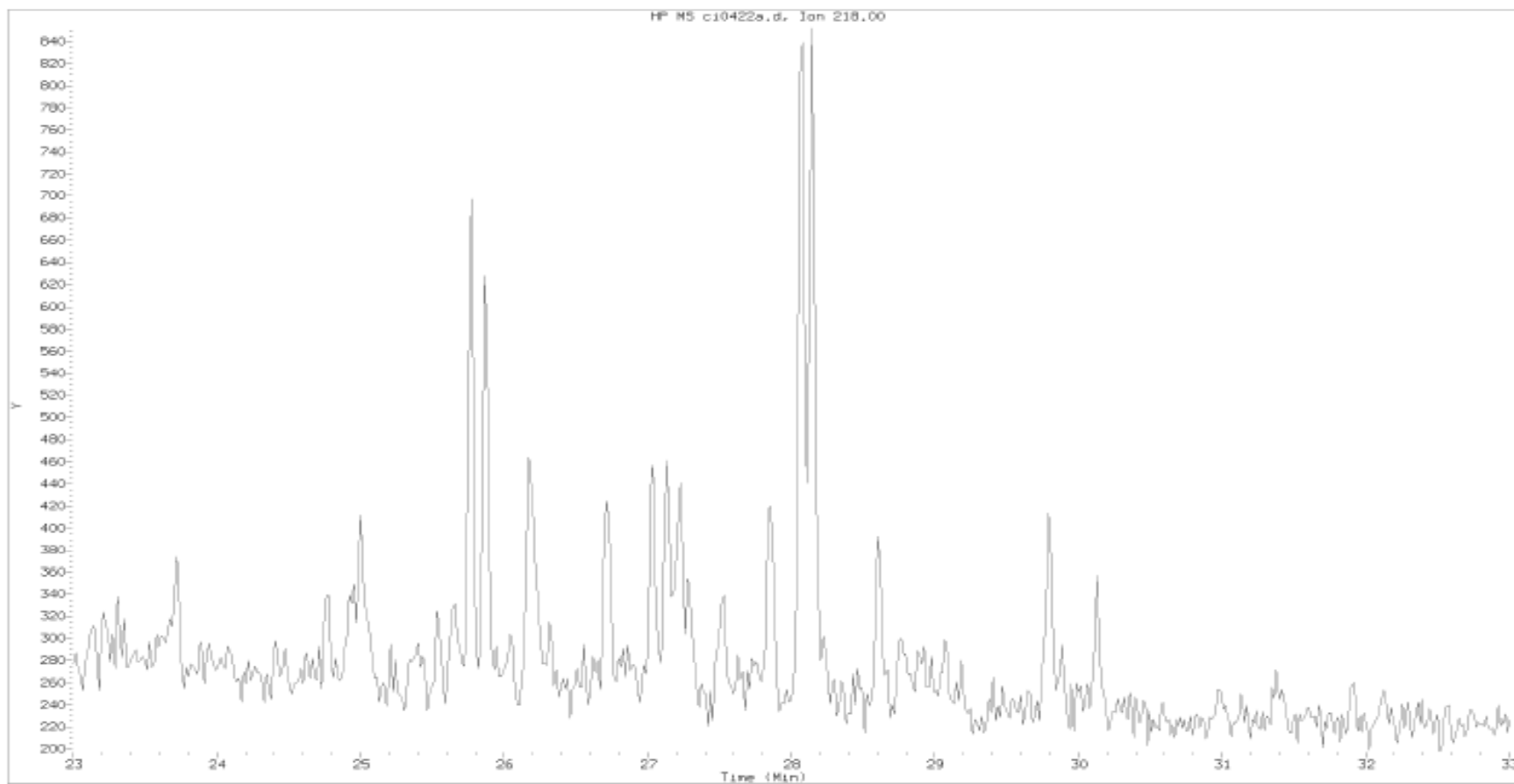
Arabian Light – Mass 191 amu EICP



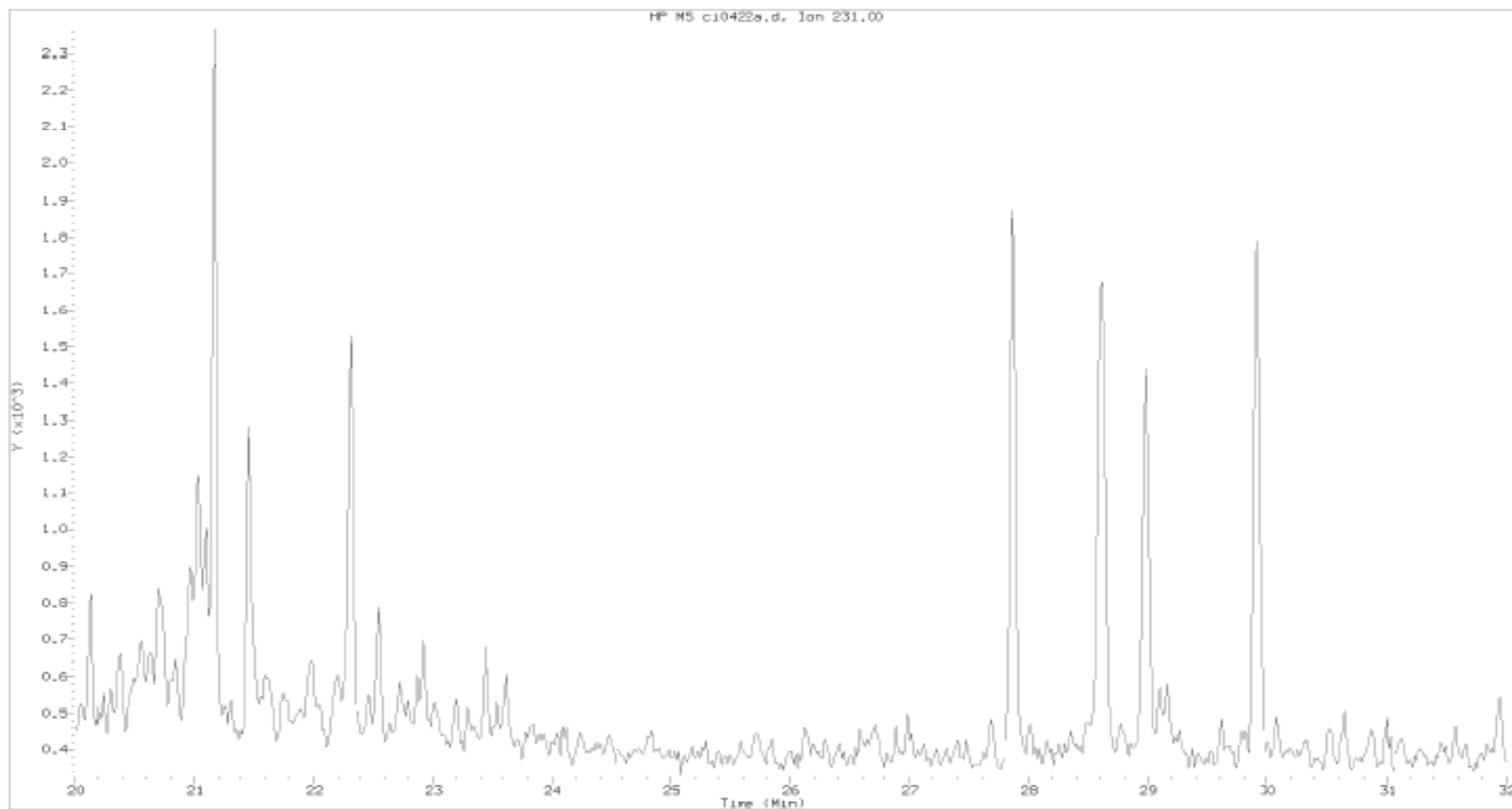
Arabian Light – Mass 217 amu EICP



Arabian Light – Mass 218 amu EICP



Arabian Light – Mass 231 amu EICP



Diagnostic Ratios

Generate diagnostic ratios for specific pairs of compounds within the classes of compounds

- Isoprenoids

n-heptadecane/pristane

n-octadecane/phytane

pristane/phytane

Diagnostic Ratios

- Alkylated PAHs

2-methylphenanthrene/1-methylphenanthrene

C2-Dibenzothiophenes/C2-Phenanthrenes

Retene/C4-Phenanthrenes

- Biomarkers

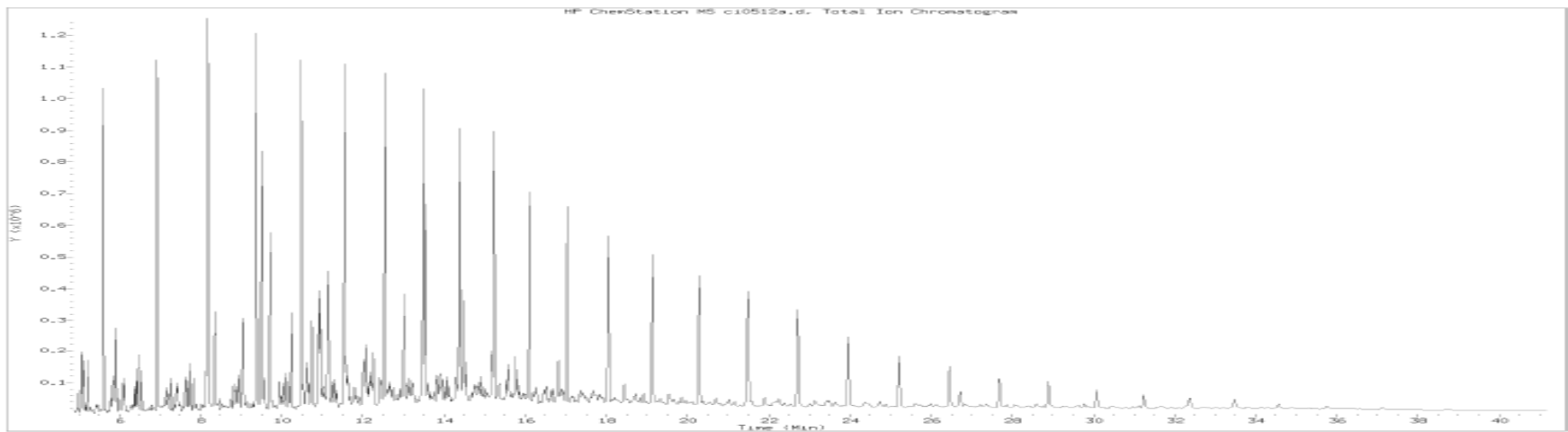
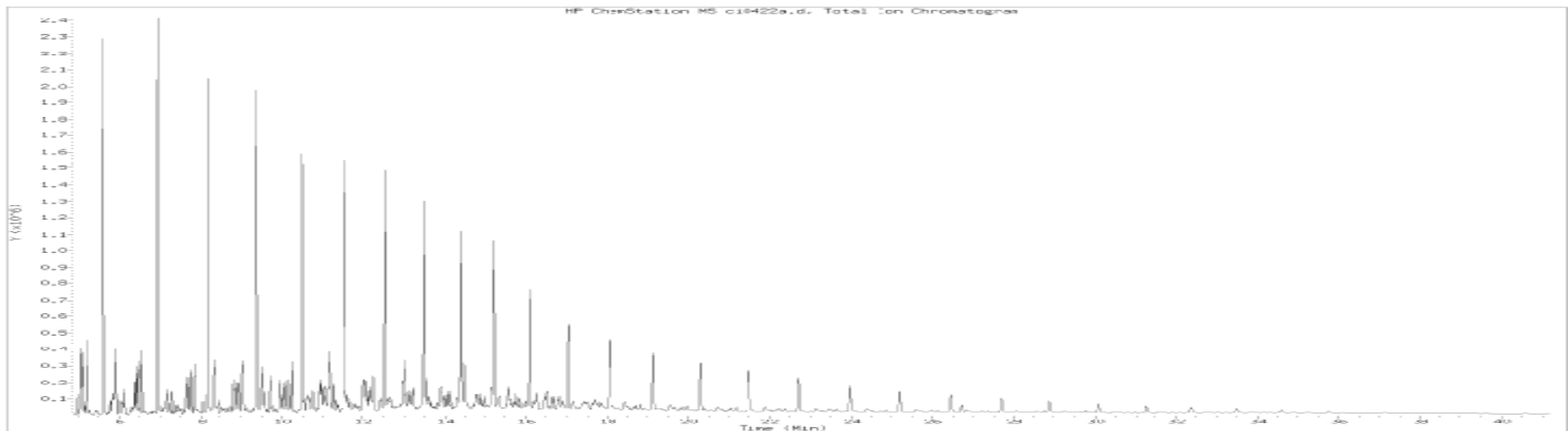
terpanes

steranes

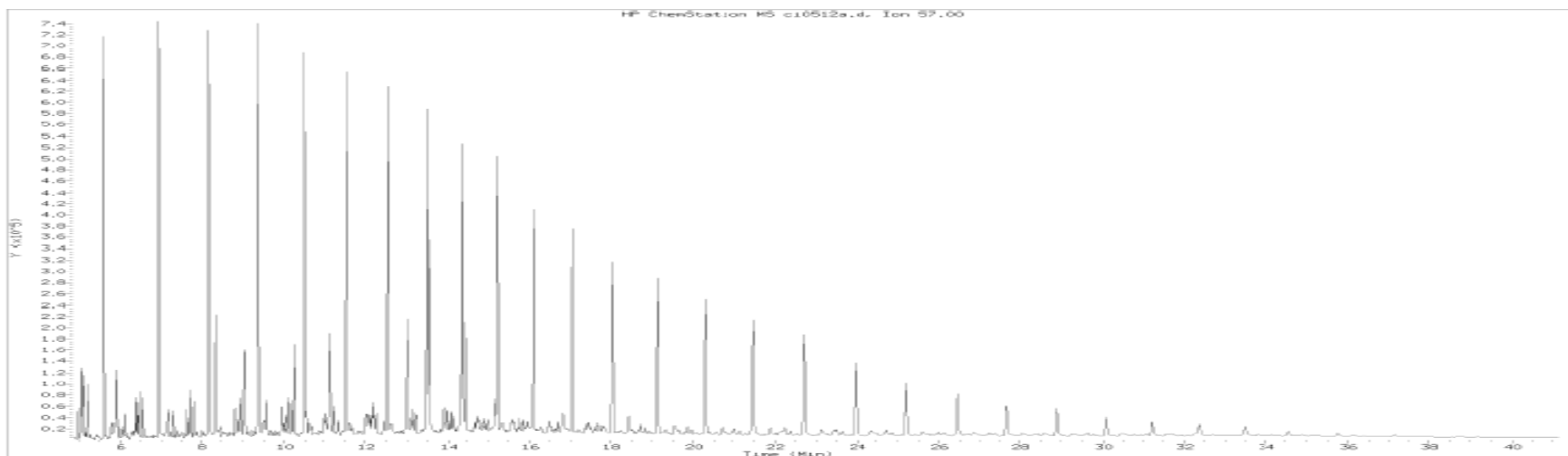
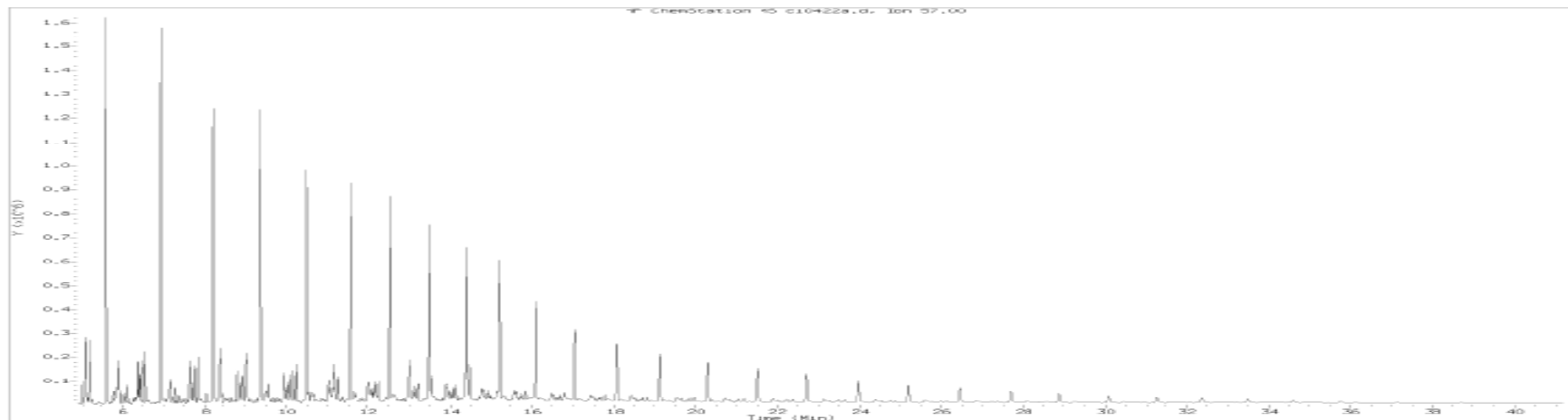
triaromatic steroids



Total Ion Chromatogram

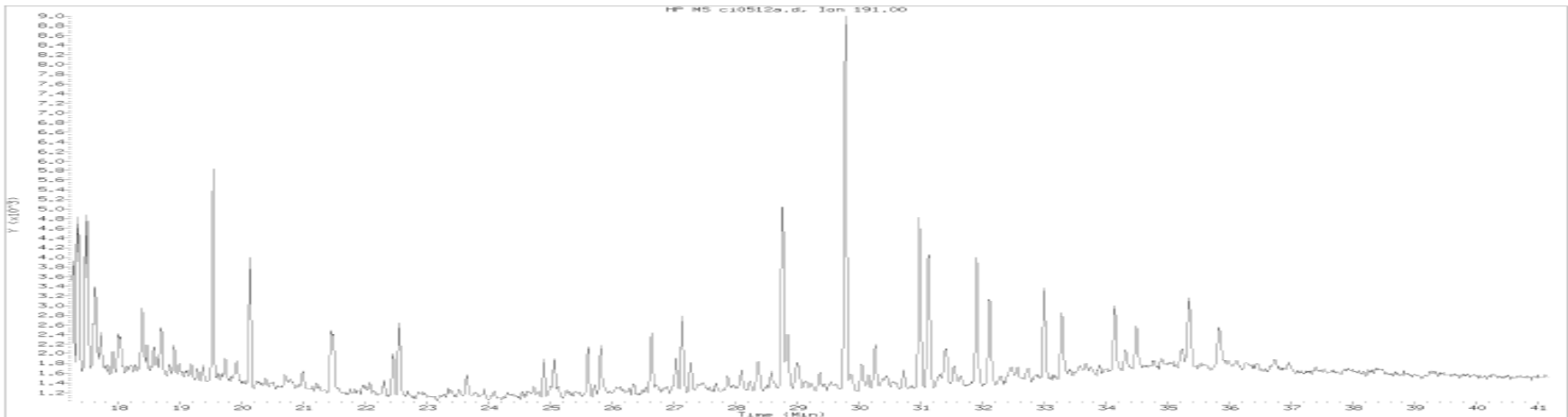
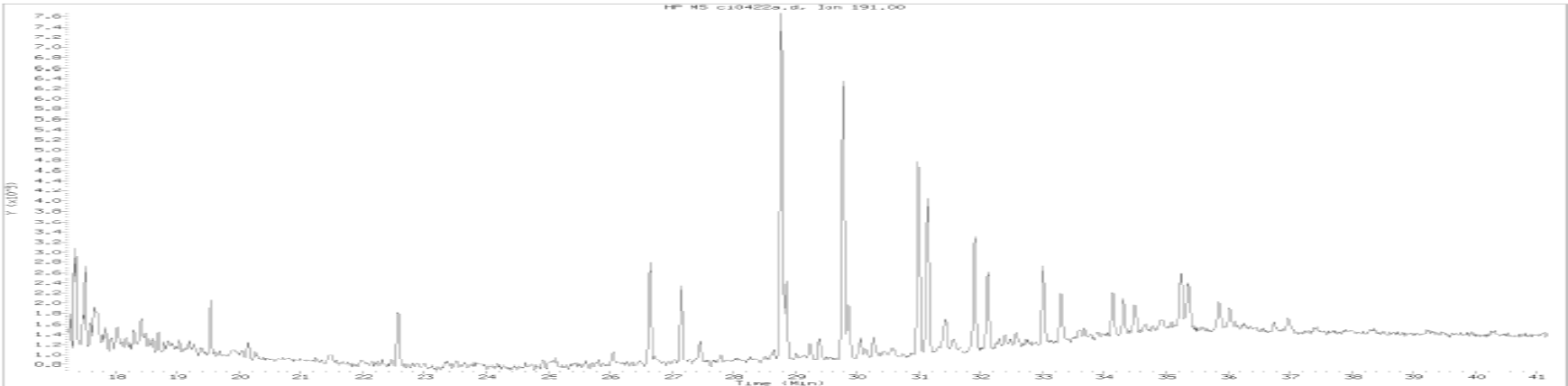


Mass 57 amu EICP

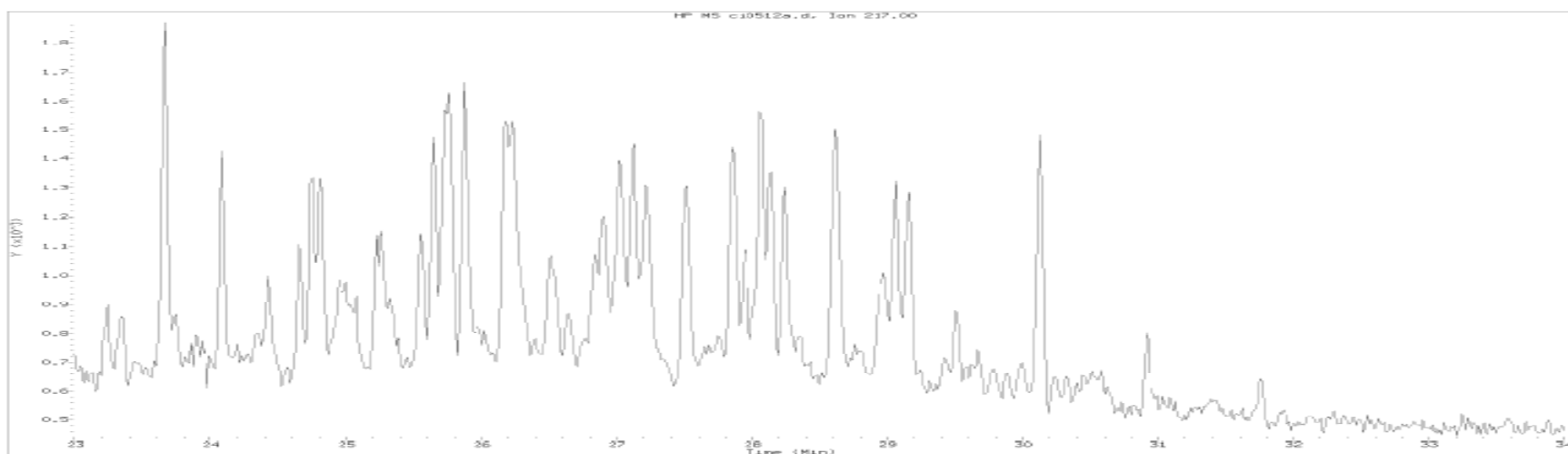
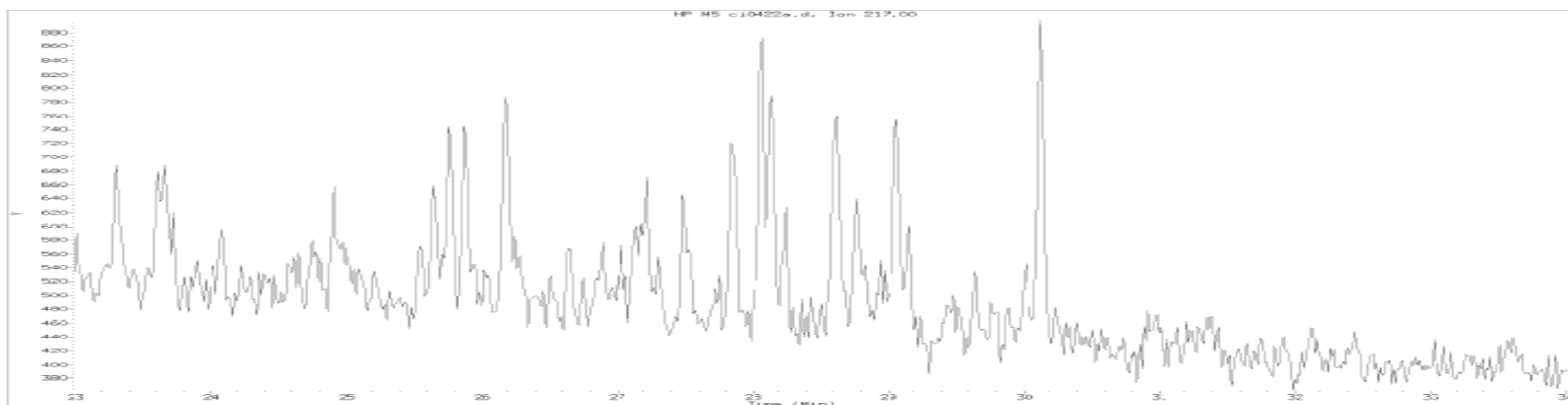




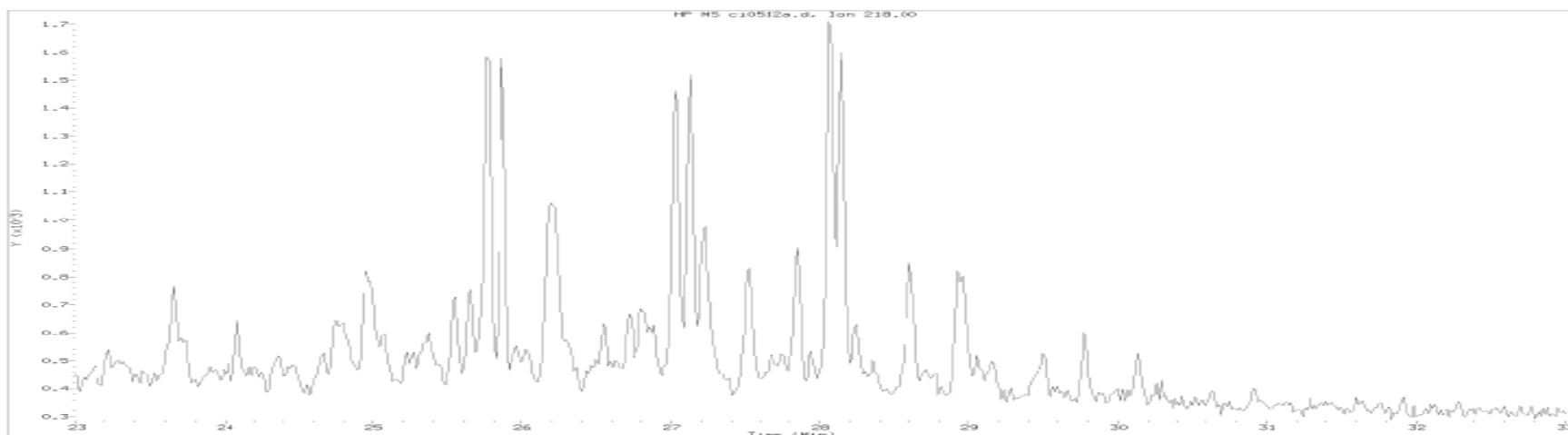
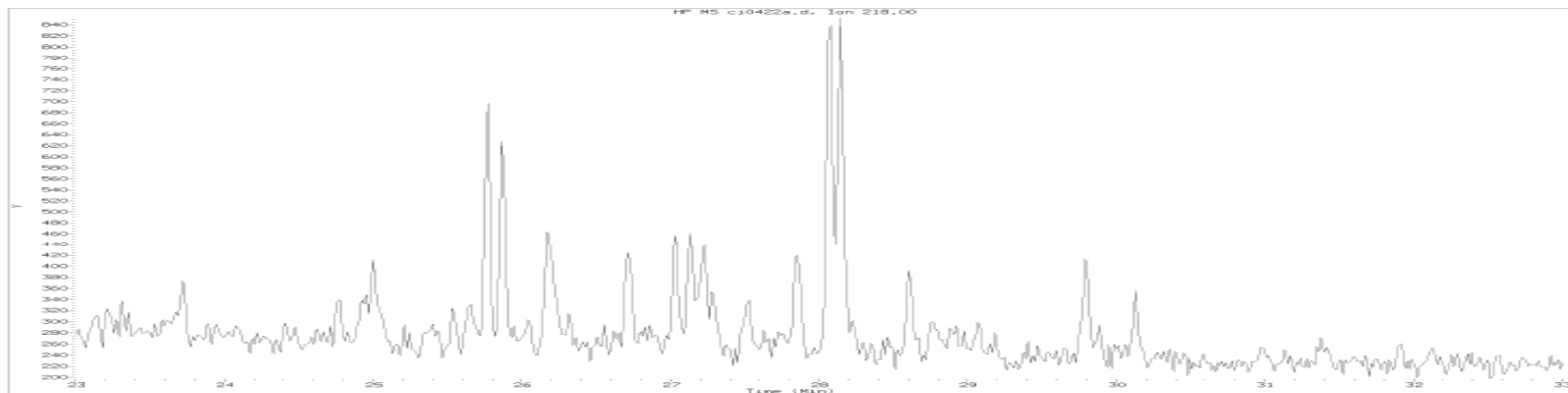
Mass 191 amu EICP



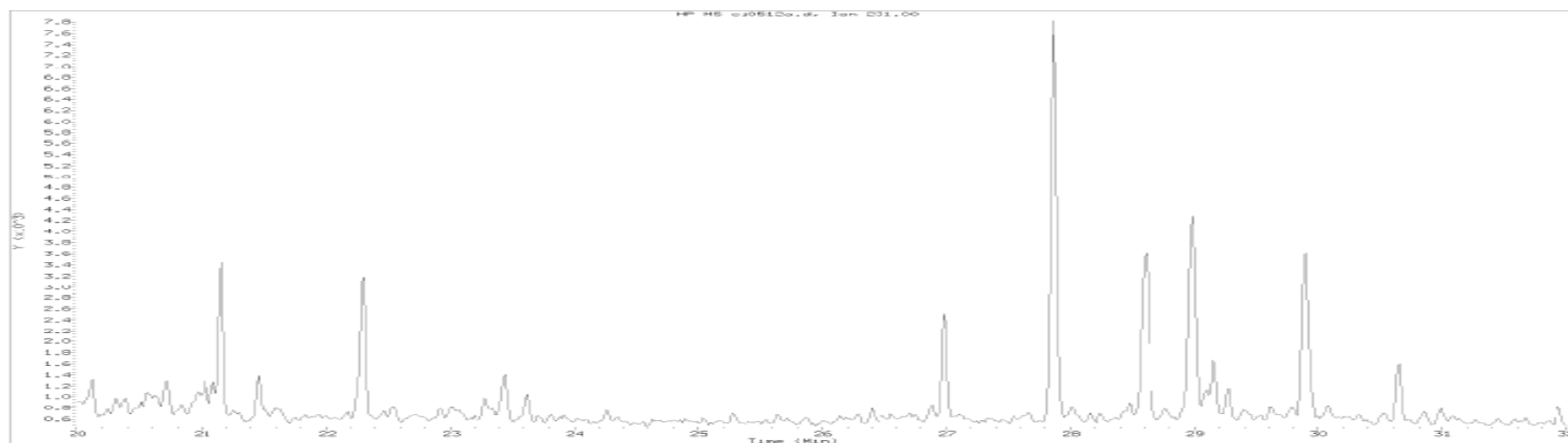
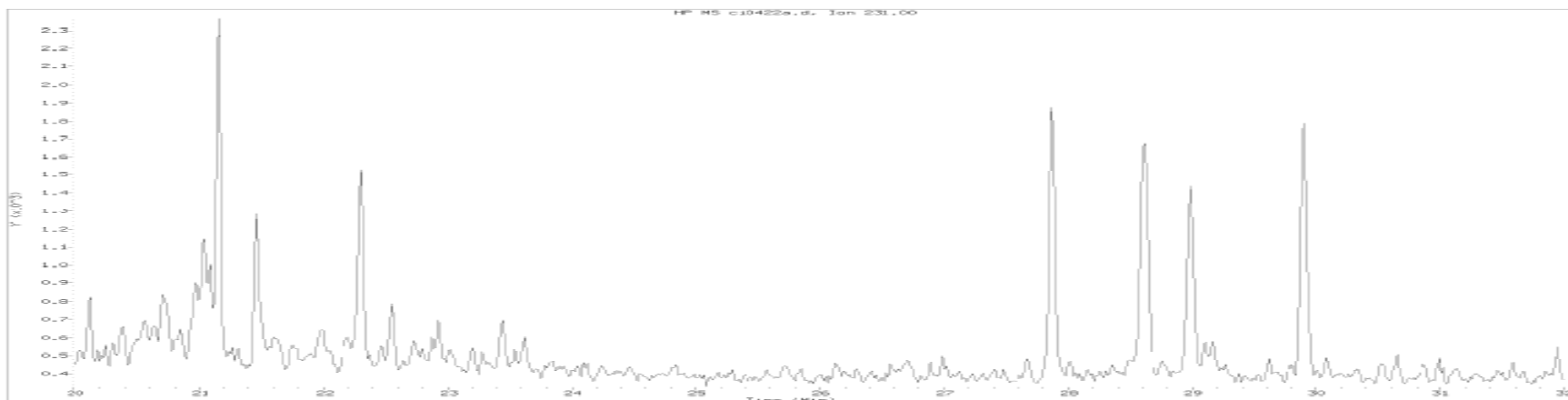
Mass 217 amu EICP



Mass 218 amu EICP



Mass 231 amu EICP



Acknowledgement

Richard Karam, Manager, Semivolatiles, Lancaster Laboratories, Inc.

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Questions ?
