TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Chemical Fingerprinting and Biomarkers (Hydrocarbon Forensics)

Rocky Mountain EHS Peer Group

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Agenda

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- Introduction
- Why do we need Chemical Fingerprinting ?
- How do Products get into the Environment?
- What is necessary to perform Fingerprinting?
- Analytical Tiers
- Methods and Choices
- Laboratory Information
- Example Data
- Summary

Communication

Introduction

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- Types of Products
- Chemical Fingerprinting and Comparisons
- Hydrocarbon GW Plume Sources
- Multiple Sources
- State Agency Analytical Parameter Recommendations
- Combination of Methods

- Tiered Approach to Characterization

Why do we need Chemical Fingerprinting?

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- Characterization of Product
- Determination of Source
- Multiple Sources?
- Allocation of Liability

How do Products get into the Environment?

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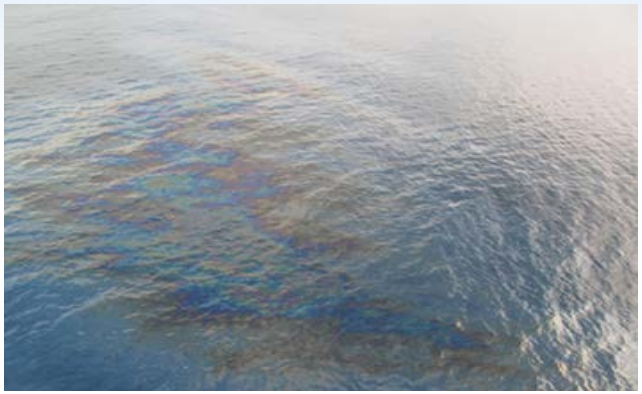
- Spills
- Leaks
- Explosions
- Natural Seeps

(6500-7000 GPD)(NOAA, Lorenson et al., 2011)



What is necessary to perform Fingerprinting?

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- Samples from Site
- Source Product or Products
- Historical Background
- All other Information

MORE INFORMATION THE BETTER !!!

Analytical Tiers

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- Tier I – GC/FID*
- Tier II – GC/MS (SHC's, PAH/APAH's, BIOMARKERS, PIANO)
- Tier III – CSIA (Carbon Stable Isotope Analysis)

- *Fuels comparison
- Whole Oil Analysis (GC/FID)

P (Paraffins), I (Isoparaffins), A (Aromatics), N (Naphthenes), O (Olefins)

Methods and Choices

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Volatiles (VOA)

- GC/FID
- GC/MS
- SW846 8015 Mod.
- SW846 8260 Mod.
- SW 846 8270D Mod.
- ASTM D7900 (Detailed Hydrocarbon Analysis (DHA))
- ASTM D6730 Mod. (DHA Analysis)
- ASTM D8003 HPLIS (n-C1 through n-C24)
- Organic Lead, Manganese Analysis
- Sulfur Analysis (ASTM D4294…….)

Methods and Choices

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Semi Volatiles (SVOA)

- GC/FID
- GC/MS
- SW-846 8015 Mod
- ASTM D3328
- ASTM D7363
- ASTM D5739
- SW 846 8270D Mod
- SINTEF 2002
- Prep Methods
- Cleanup Methods

Quantitative method best approach

Matrices

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- Pure Product
- NAPL (Nonaqueous Phase Liquids)
- Soils & Sediments
- Water
- Matrix Combinations

Factors Affecting Fingerprinting

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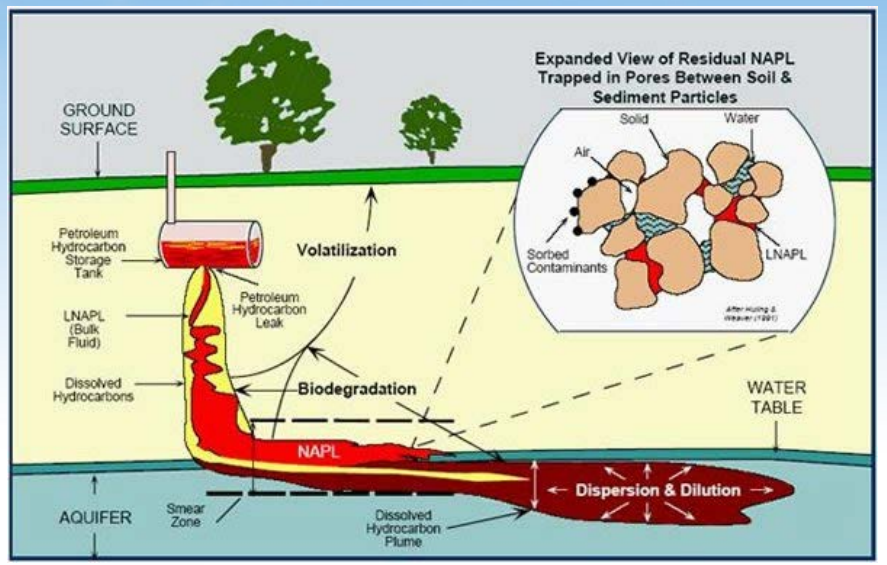
- Weathering
- Evaporation
- Water Washing
- Biodegradation
- Additives and Blending
- Crude Oil Genesis
- Petroleum Refining
- Mixing in the Environment



Naturally Occurring Sources and Anthropogenic Sources

Techniques

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- Fingerprints
- Diagnostic ratios
- Models, Statistics, Chemo metrics
- Mapping and Visualization

Data Presentation

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- Quantitation Reports
- GC/FID traces
- Total Ion Chromatograms
- Weathering patterns
- Diagnostic ratios – Isoprenoids, PAH's/APAH's, Biomarkers
- Histograms – SHC's, PAH's/APAH's, Biomarkers, Metals
- Determination of processes (Petrogenic, Pyrogenic, Biogenic)
- Scatter Plots, Radar Plots (PIANO Components)
- Principal Component Analysis (PCA)
- Data Interpretation Reports

Example Data – GC/FID Traces

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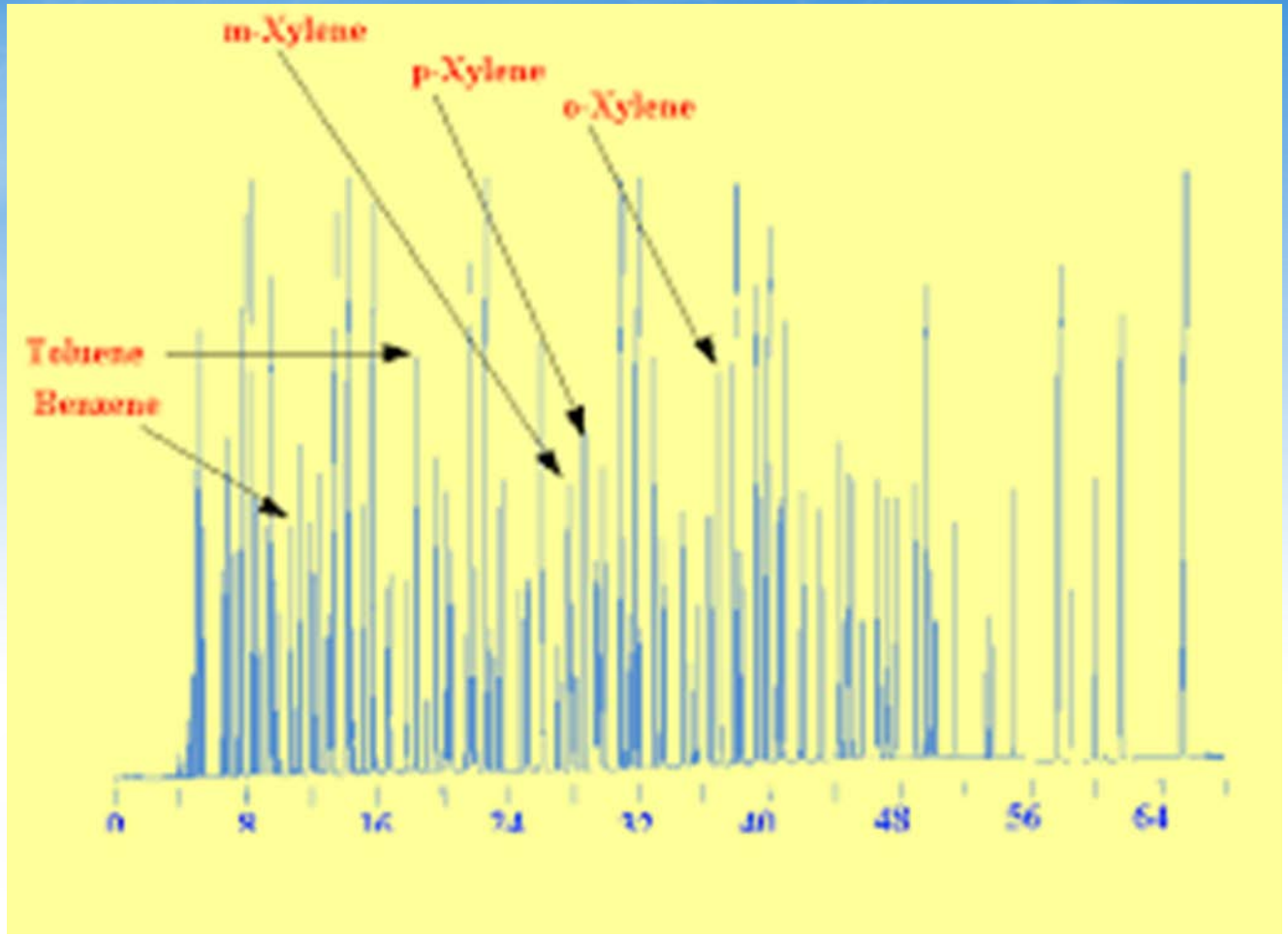

Example Data - Overlays

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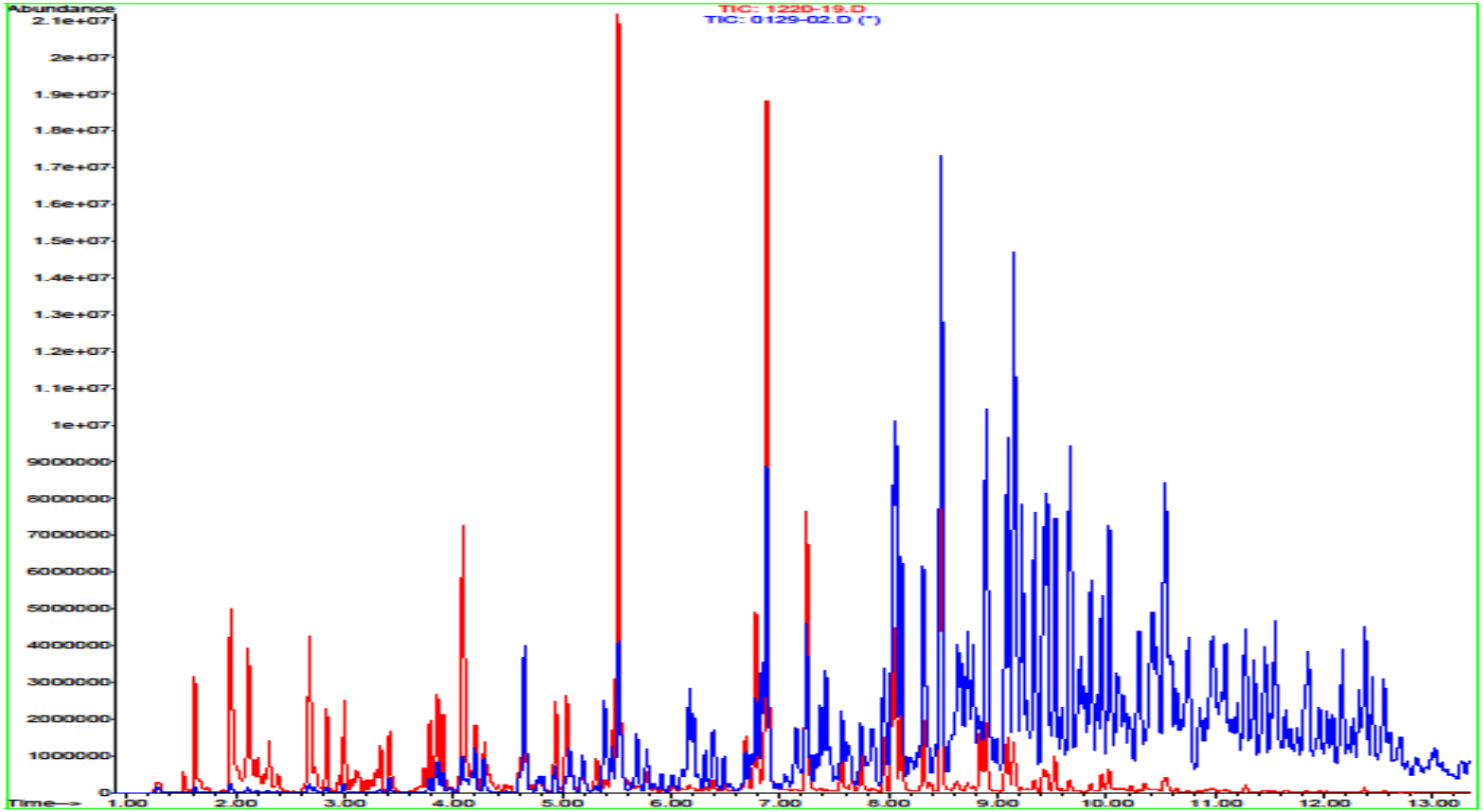
```
File          : C:\MSDCHEM\1\DATA\122017\1220-19.D
Operator      : JRV
Acquired      : 20 Dec 2017    9:54 pm using AcqMethod DEFAULT
Instrument    :
    HP48
Sample Name:  STD4000
Misc Info     : 490-0101291-019
Vial Number:  19
```



Example Data – Weathering patterns

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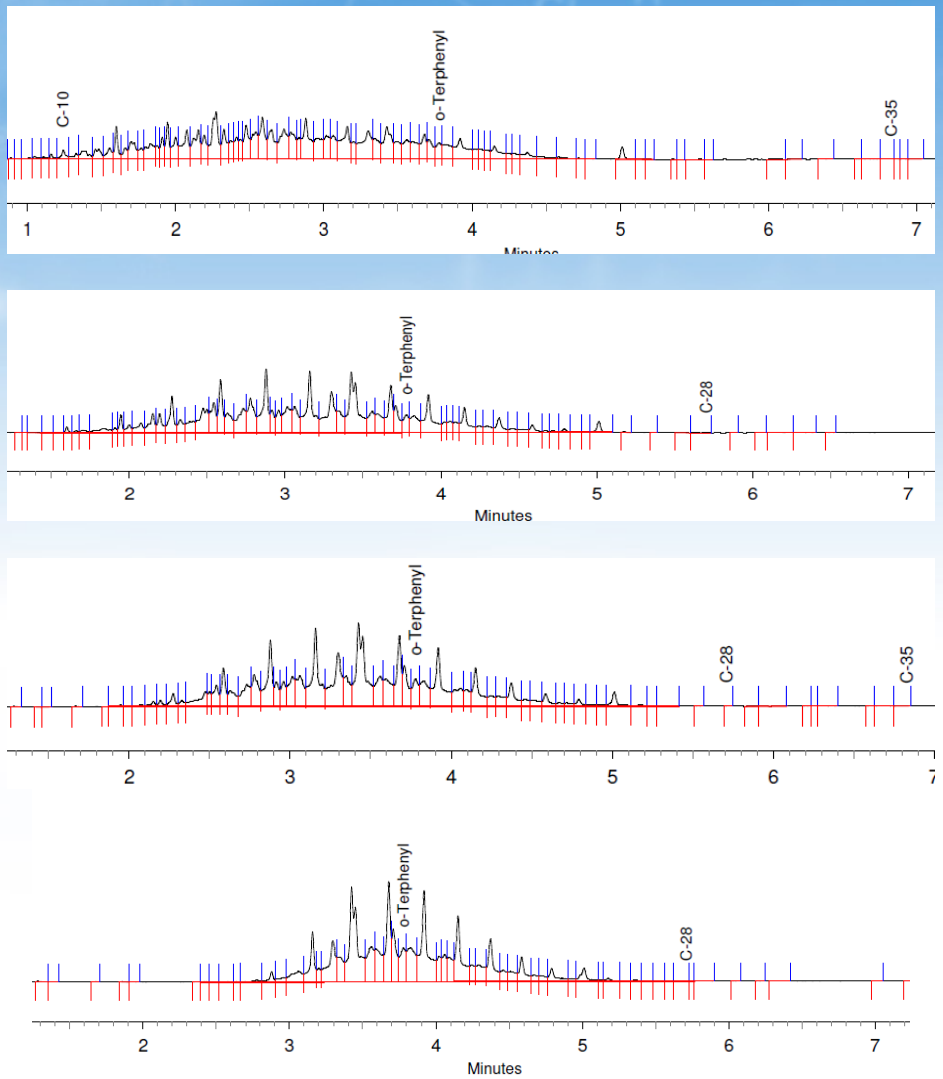

Example Data – Weathering patterns

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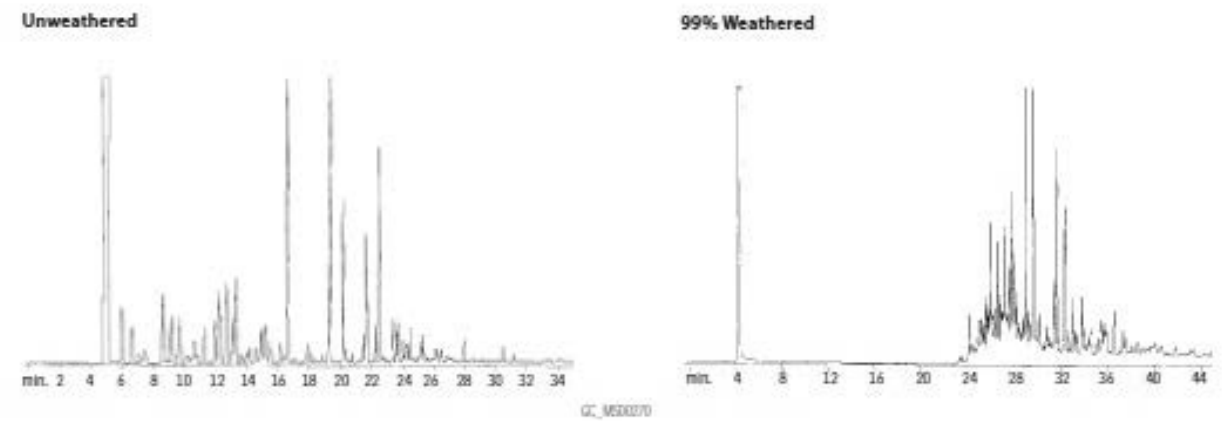
Unleaded Gasoline
Rtx®-1



30m, 0.53mm ID, 1.50µm Rtx®-1 (cat.# 10170)
Oven temp.: 40°C (hold 3 min.) to 75°C @ 15°C/min. to 275°C @ 20°C/min. (hold 5 min.)
Inj./det. temp.: 250°C/285°C
Carrier gas: hydrogen
Linear velocity: 50cm/sec. set @ 40°C
FID sensitivity: 4.10 x 10⁻¹ AFS
Split ratio: 30:1

Restek Corporation 110 Benner Circle Bellefonte, PA 16823
814-353-1300 • 800-356-1688 • Fax: 814-353-1309 • www.restek.com

Example Data - PIANO

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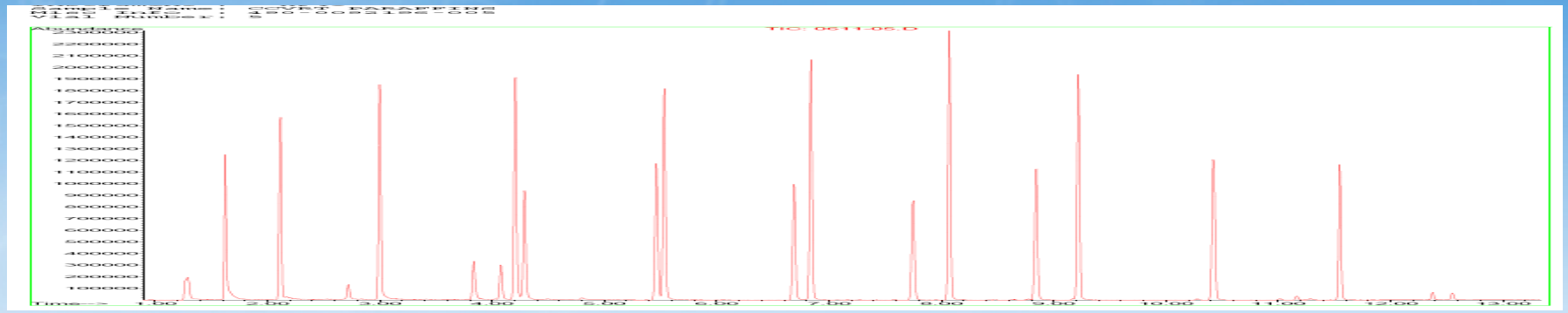
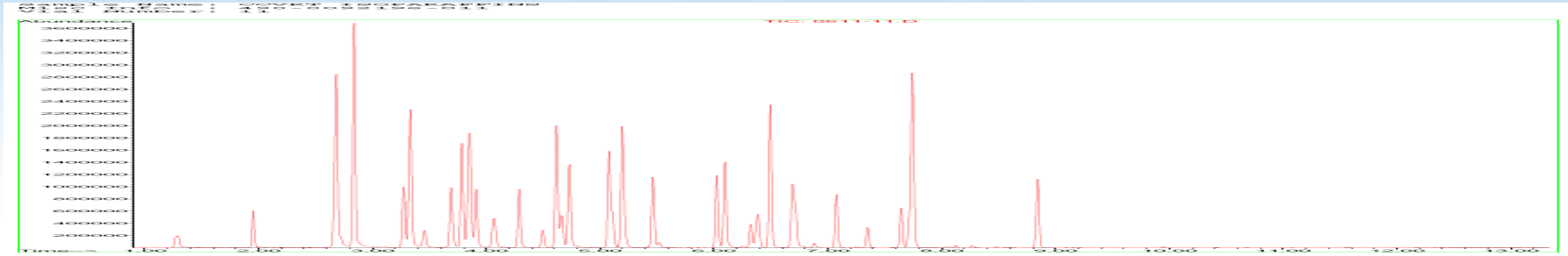
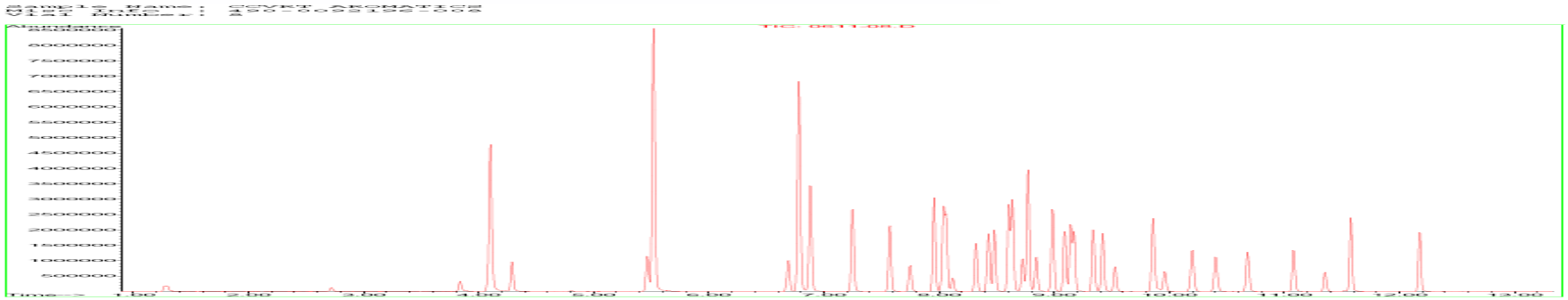
- PIANO - GC/MS 8260 (Paraffins, Isoparaffins, Aromatics)







Example Data – PIANO

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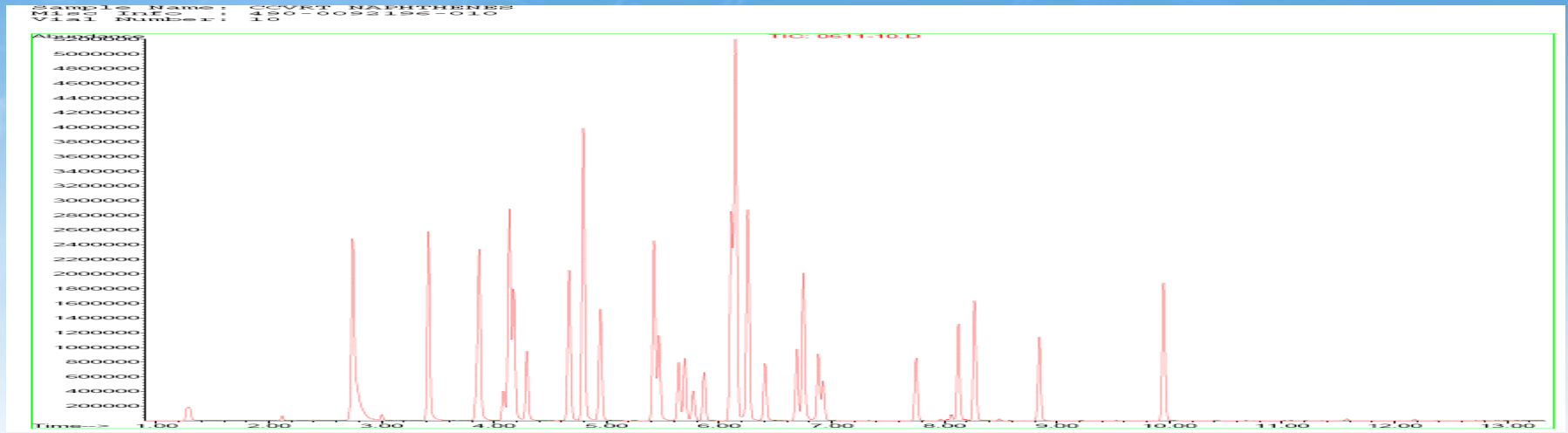
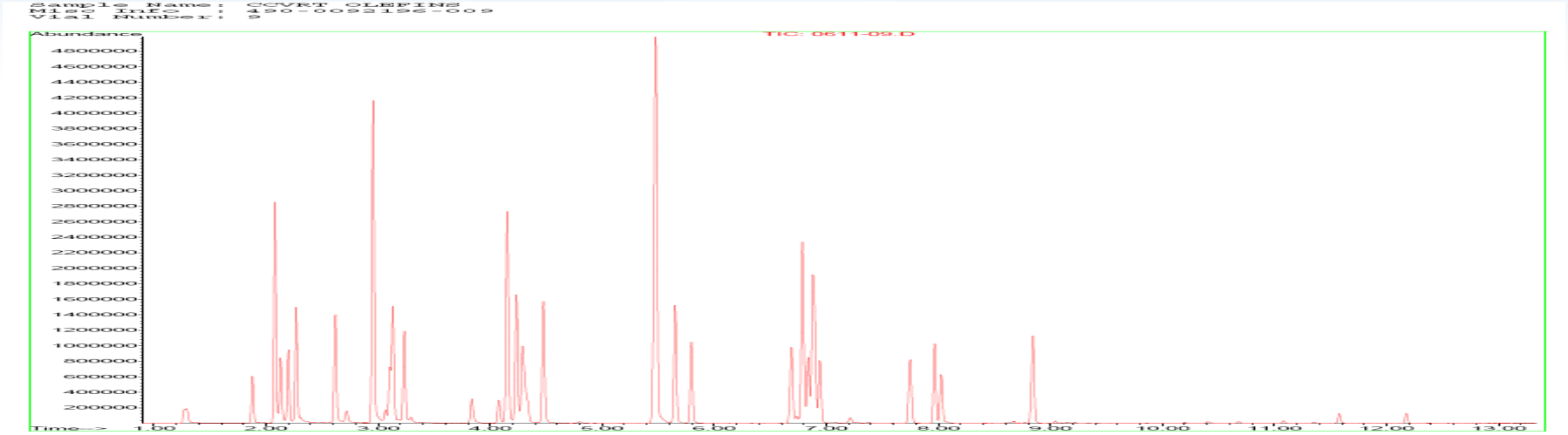
- PIANO - GC/MS 8260 (Naphthenes & Olefins)





Example Data – Diagnostic Ratios

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Isoprenoid Ratios

- n-C17/Pristane
- n-C18/Phytane
- Pristane/Phytane
- n-C17/n-C18

PAH's

C2 DBT/C2 PHE
C3 DBT/C3 PHE
C3 DBT/C3 CHR

Example Data – Diagnostic Ratios

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Isomerization
Isopentane / Pentane
2-Methylpentane / 3-Methylpentane
Evaporation
n-Pentane / n-Heptane
2-Methylpentane / 2-Methylheptane
Water Washing
Benzene / Cyclohexane
Toluene / Methylcyclohexane
Aromatics / Total Paraffins
Aromatics / Naphthenes
Benzene / Toluene
Toluene / Total Xylenes
Biodegradation
(C4 - C8 Paraffins + Isoparaffins) / C4 - C8 Olefins
3-Methylhexane / n-Heptane
Methylcyclohexane / n-Heptane
Isoparaffins + Naphthenes / Paraffins
Octane Rating / Alkylation
2,2,4,-Trimethylpentane / Methylcyclohexane
Refining Ratios
2,2,4 - TMP+Toluene / n-C7 + n-C8
2,2,4 - TMP / (2,2,4 - TMP + 2,2,3 - TMP + 2,3,4 - TMP + 2,3,3 - TMP)
n-C4/(n-C4 + i-C4)
i-C5/(i- C5 + n- C5)
Naphthalene/n-C12
Note: TMP = Trimethylpentane

Example Data - Histograms

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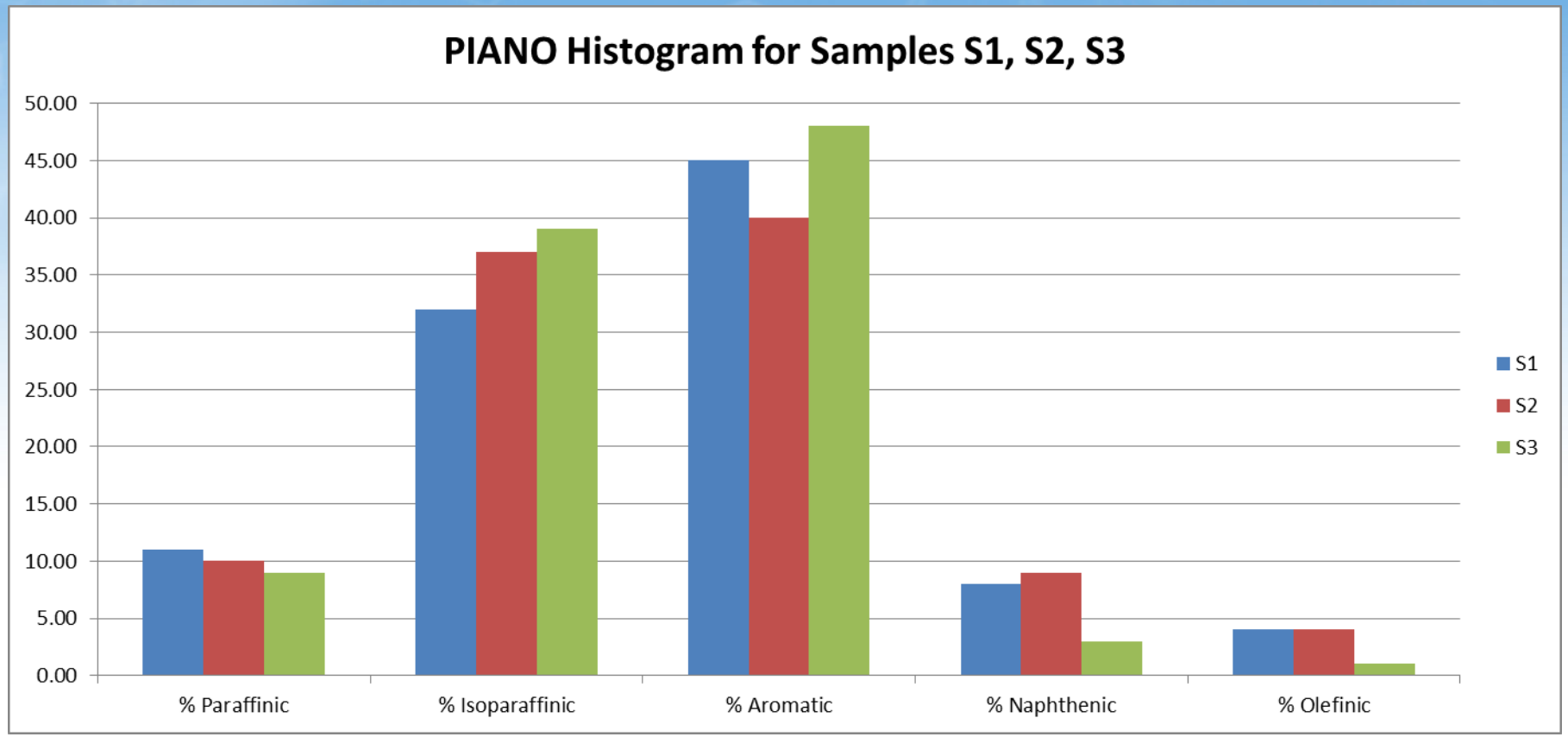

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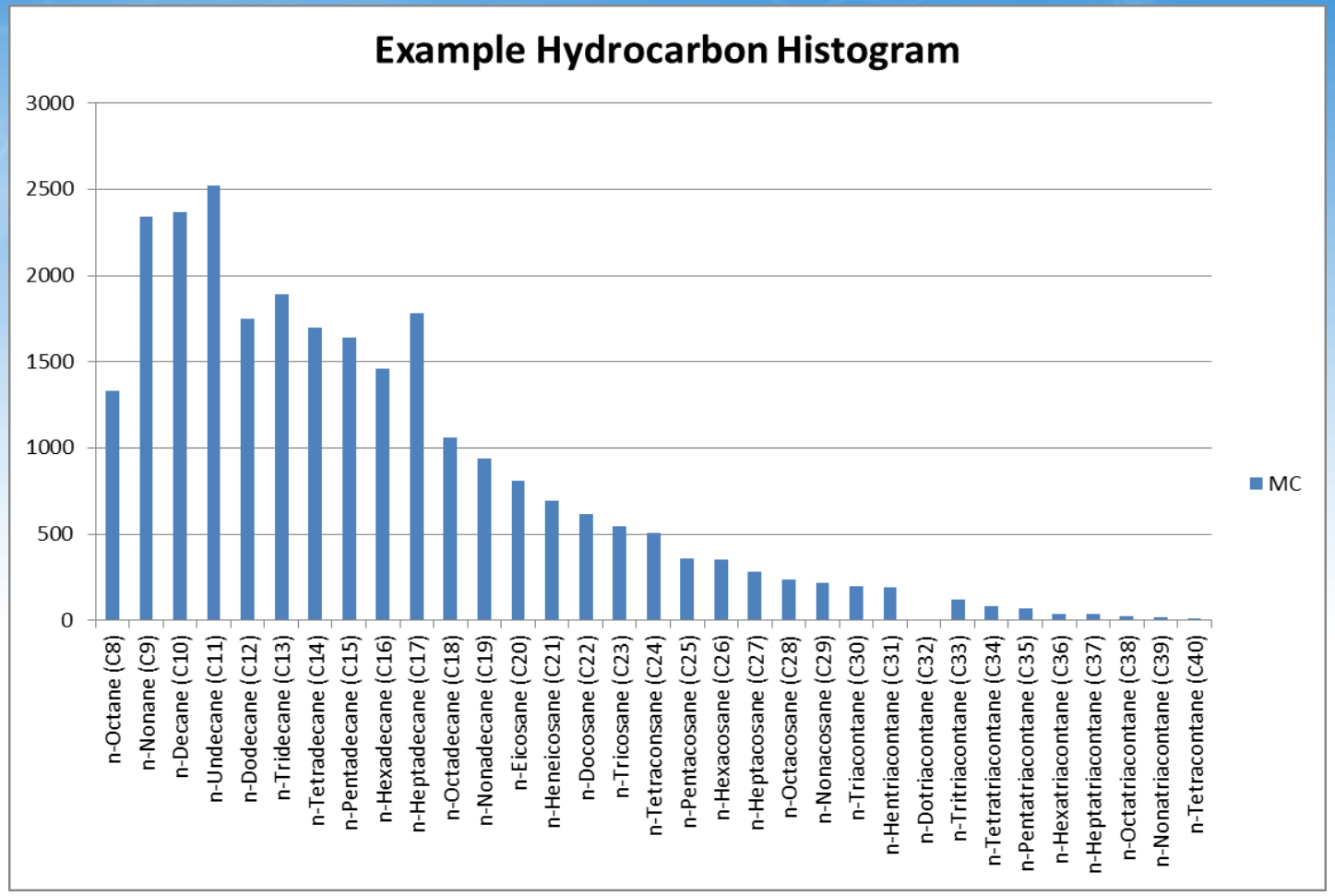

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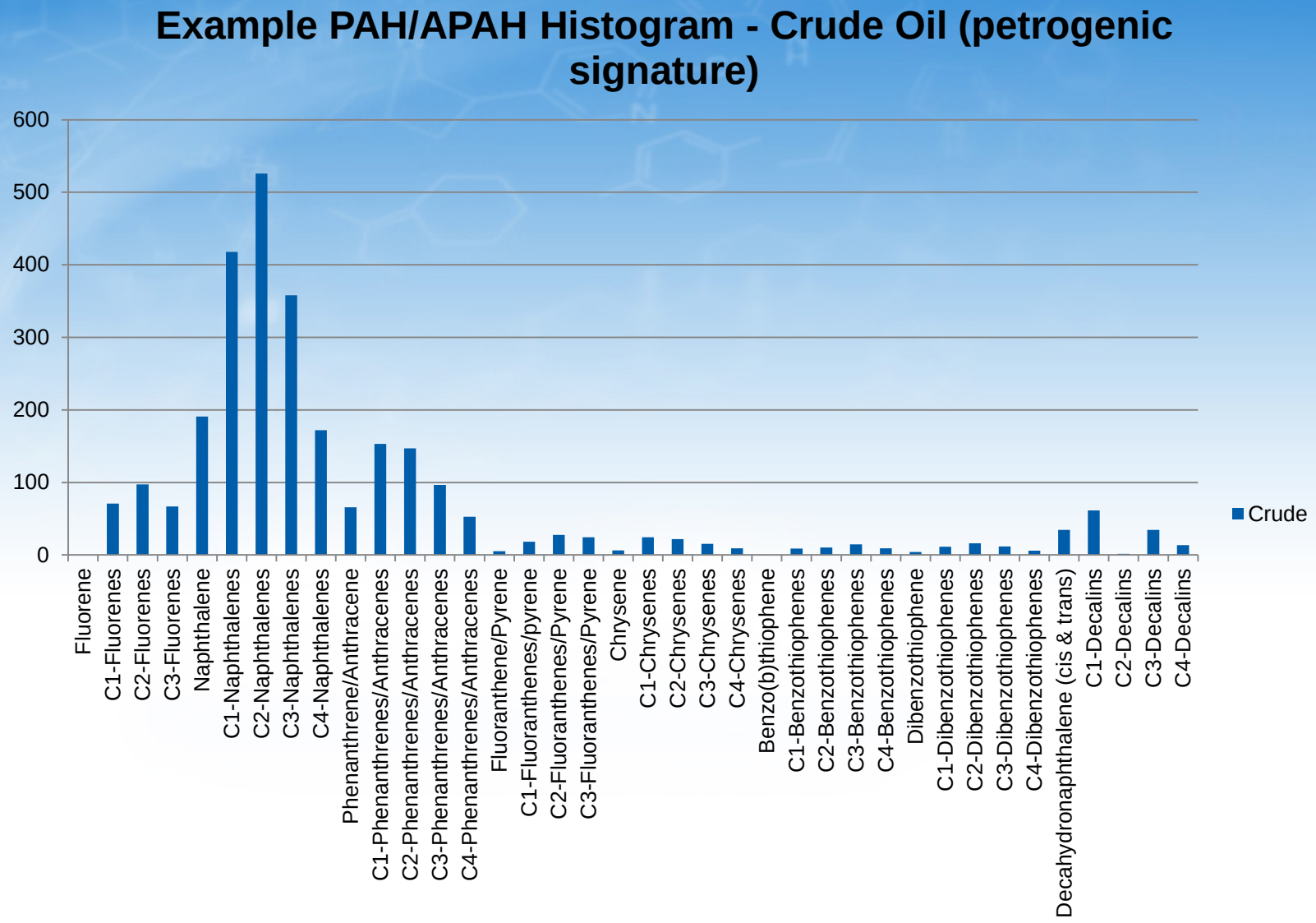

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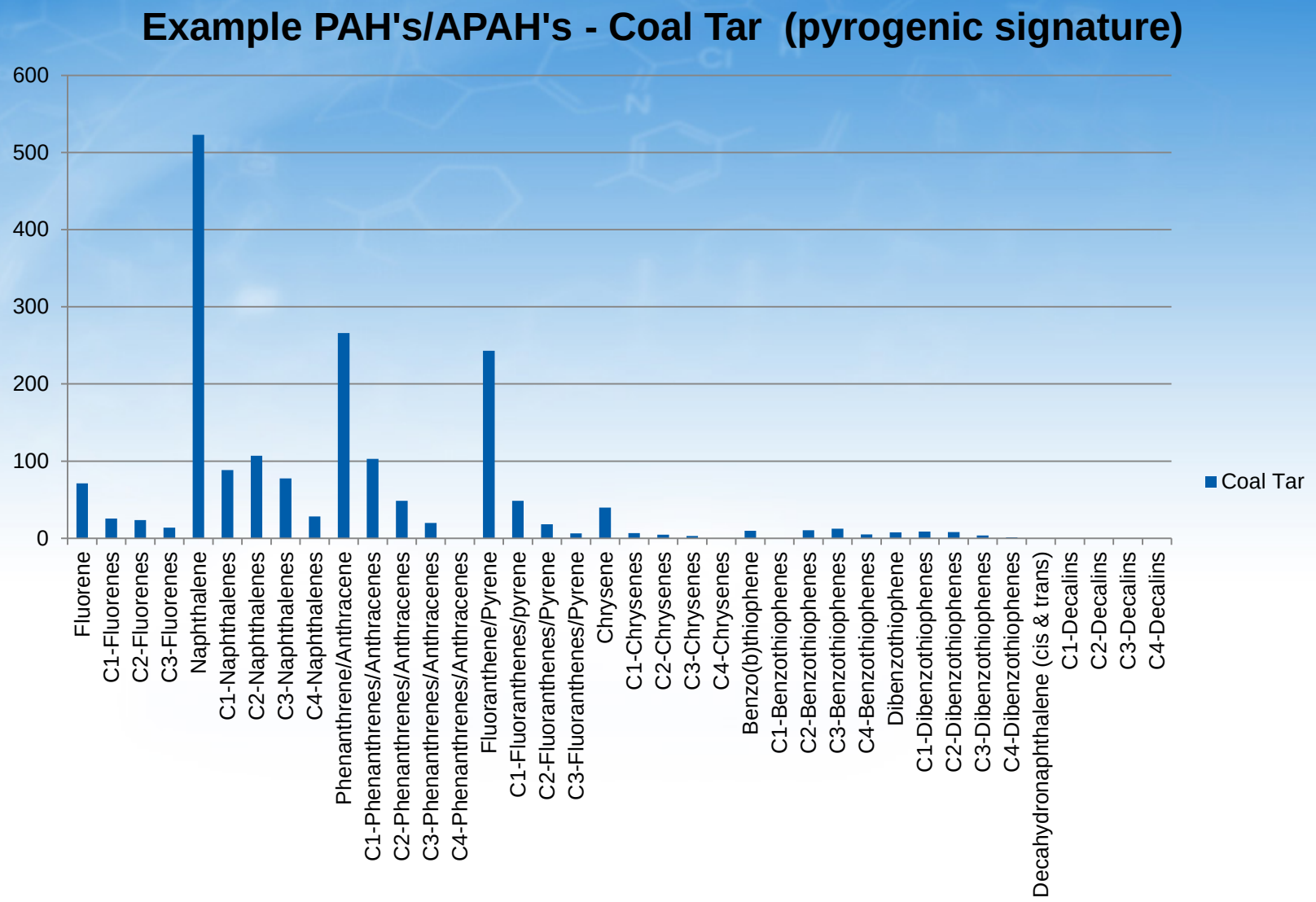

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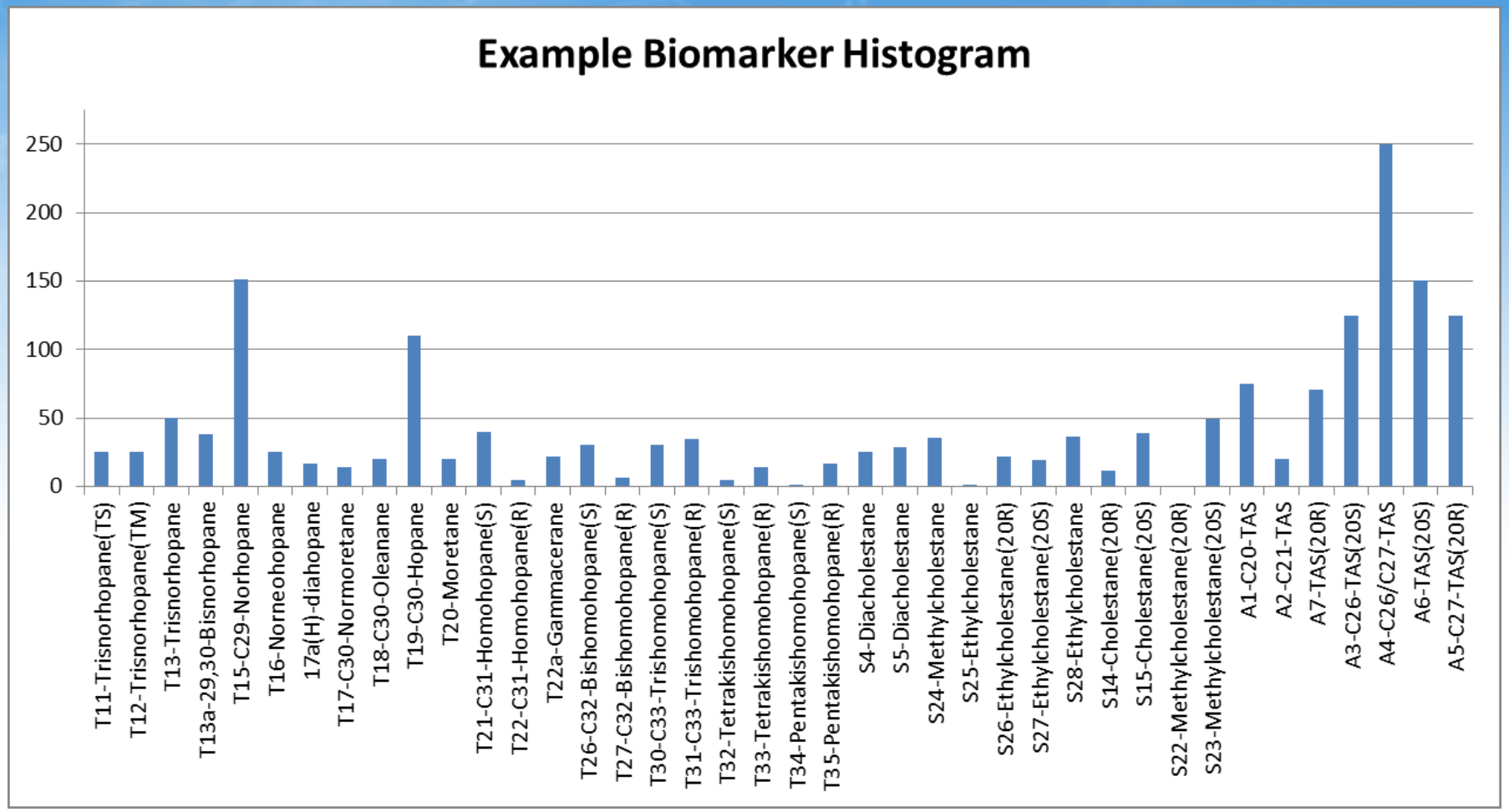

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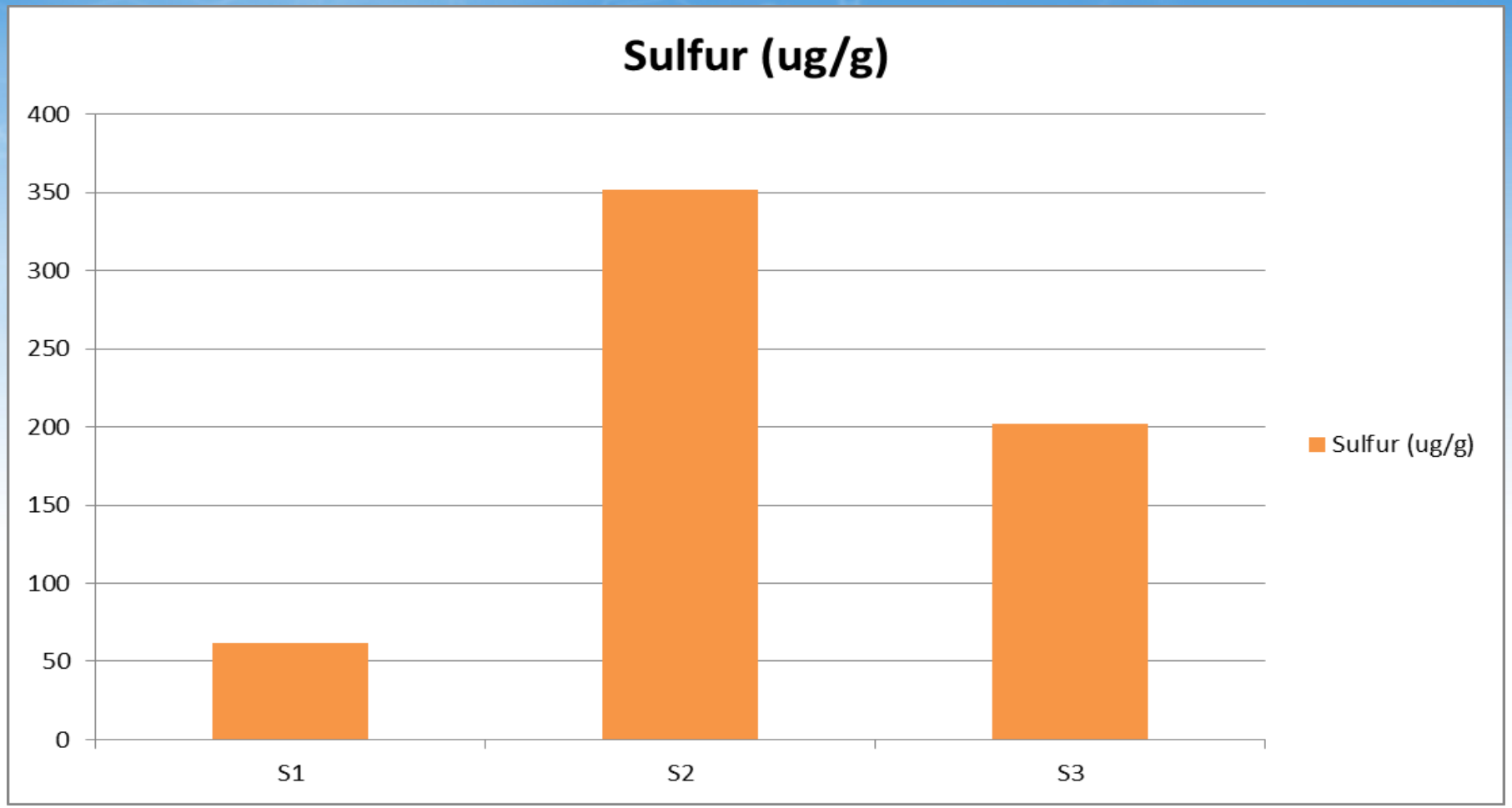

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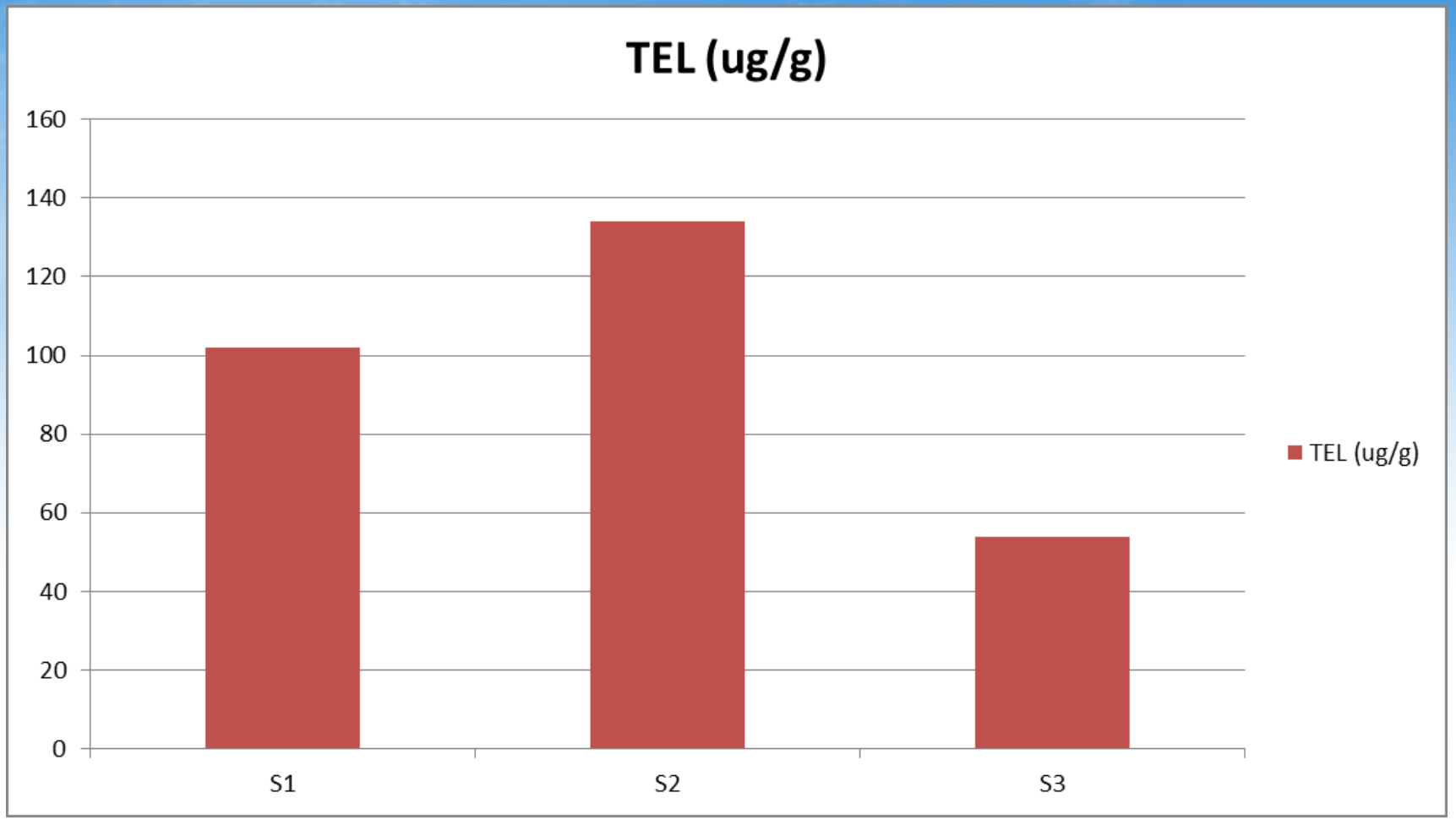

Example Data – Radar Plot

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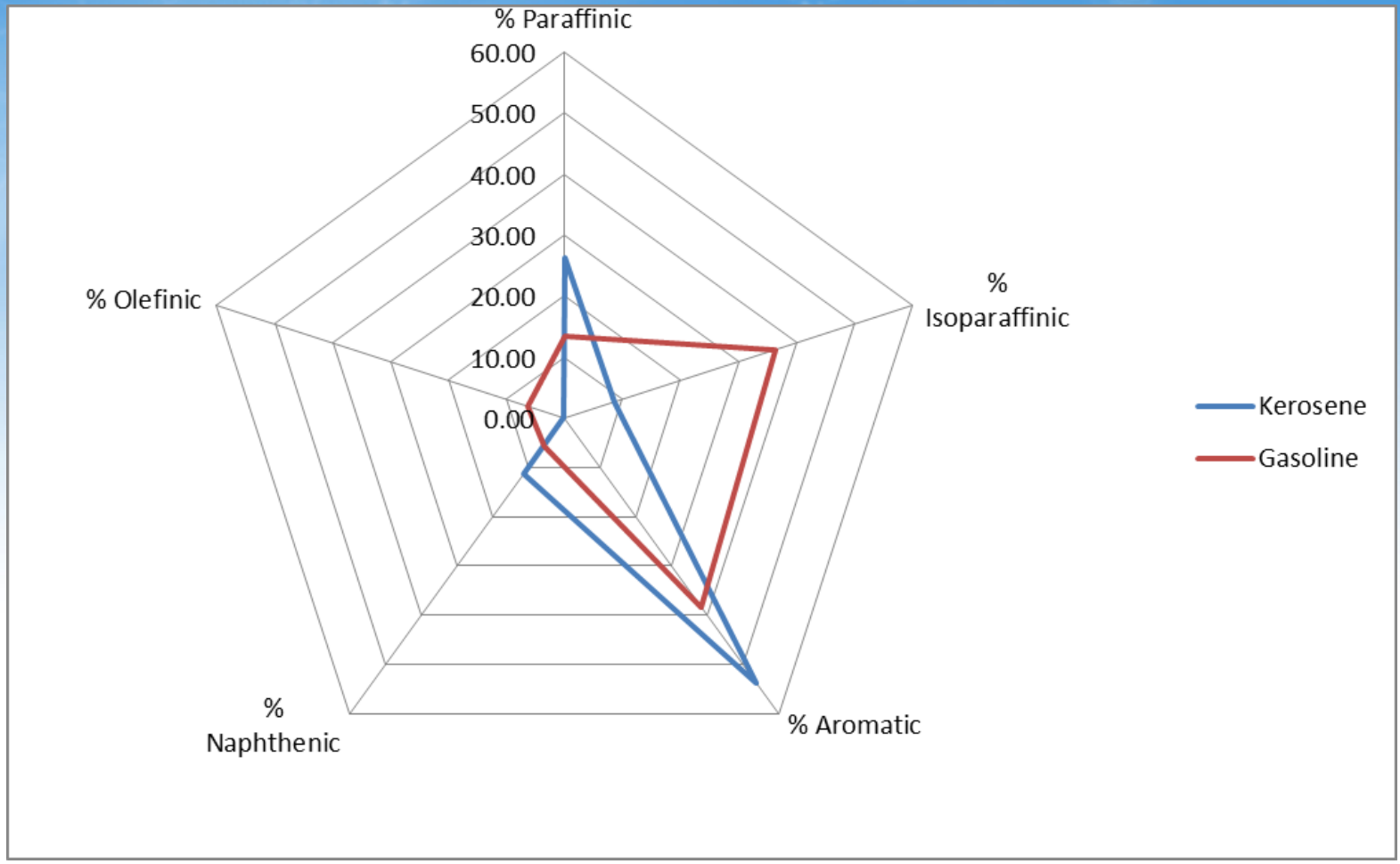

Summary

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- Analysis is complicated
- Methods are standard with modifications
- Must understand the overall history
- Must know the site well and its documentation
- Multiple sources always a problem
- Source and Library of Components Necessary
- Multiple Paths for Data Interpretation
- Interpretation consists of visual and quantitative techniques
- Cannot provide rush TATs like the traditional analyses
- Lots of Information Needed !!!!!

References

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