New Methods to more Accurately Quantify Hydrocarbon Contamination from Natural Background

AGAT Laboratories

Service Beyond Analysis

www.agatlabs.com

Overview

- Environmental Forensics
- GCxGC
  - Principles
  - Benefits
  - Uses
  - Outputs and Analysis
- Biogenic Analysis by GCxGC-FID
  - Method of analysis
  - Project examples
- Future Work

Environmental Forensics

- Reconstructs events in the environment using defensible scientific methods to differentiate between complex compounds found in the environment.

- This provides information about the compounds present and their underlying chemistry

- This information can be used to determine many things:

    - Was the site contaminated by current activities or from some other source?
    - Was the site contaminated by a previous owner/user
    - When did the contamination occur?
    - Is the contamination due to natural processes (biogenic) or an unnatural spill (petrogenic)?
    - Is there more then one source present in the contamination?

Environmental Forensics

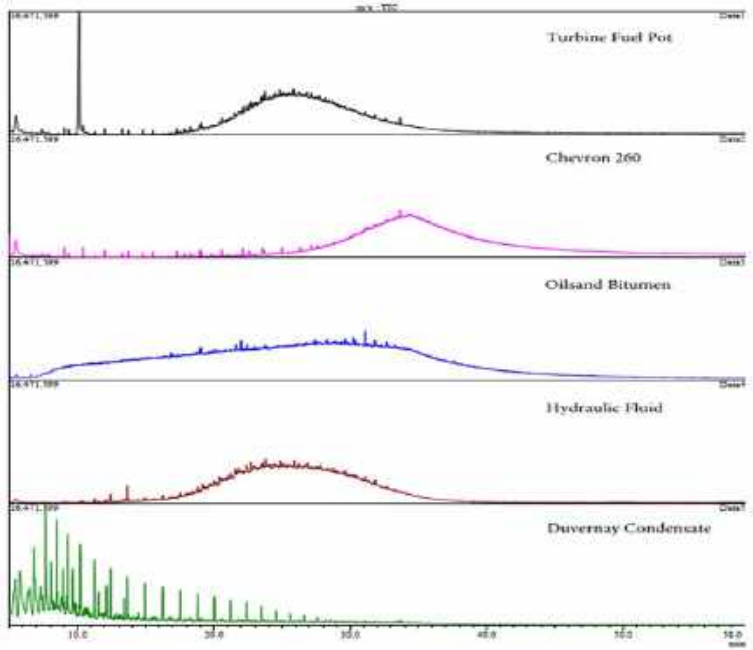
How do we determine forensic information?

Look for fingerprints

- Each hydrocarbon type has a different characteristic elution pattern on a GC
- Based on this pattern the type of fuel can be determined.

Compare the sample from the environment to known fuel to see what it matches.

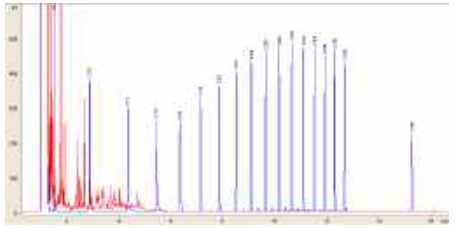
Sometimes sample is contaminated with naturally occurring hydrocarbons which can cause results to be over guidelines



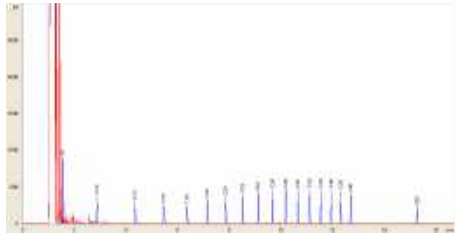
Total Ion Chromatograms (TIC) comparison of the Turbine Fuel Pot sample and comparison samples from the Agat Oil Forensic Library. The Turbine Fuel Pot sample is distinct from the other other types and most closely resembles the Hydraulic Fluid standard. The match is not exact and a further search of Hydraulic Fluids and Gear Oils used at the sample site may identify the unknown matching product.

Environmental Forensics

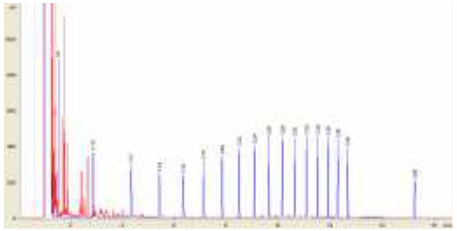
Fresh Gasoline



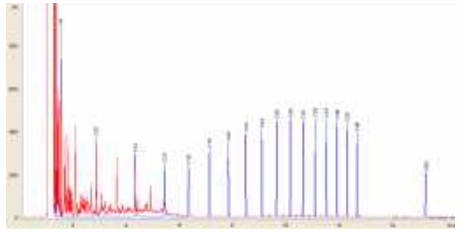
Aviation Gasoline



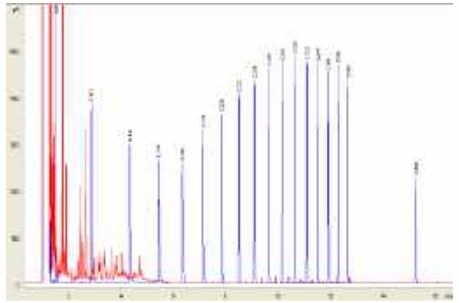
Weathered Gasoline



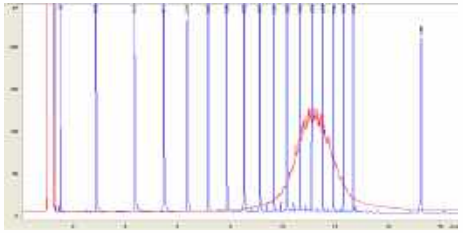
Jet Fuel A



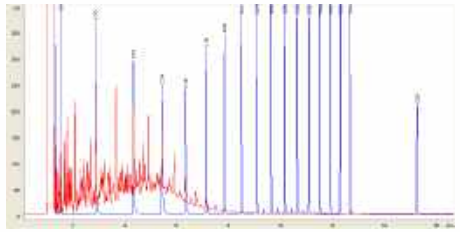
Unknown



New Motor Oil

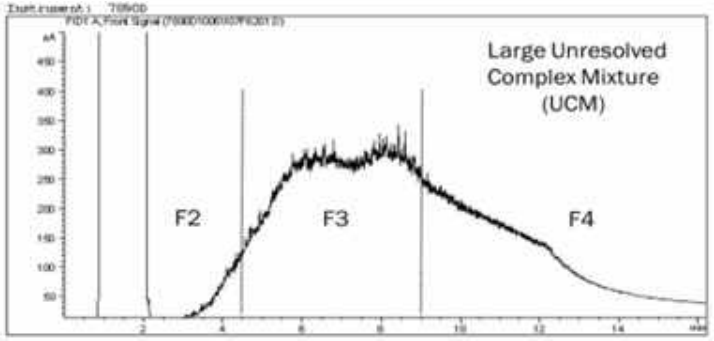


Diesel

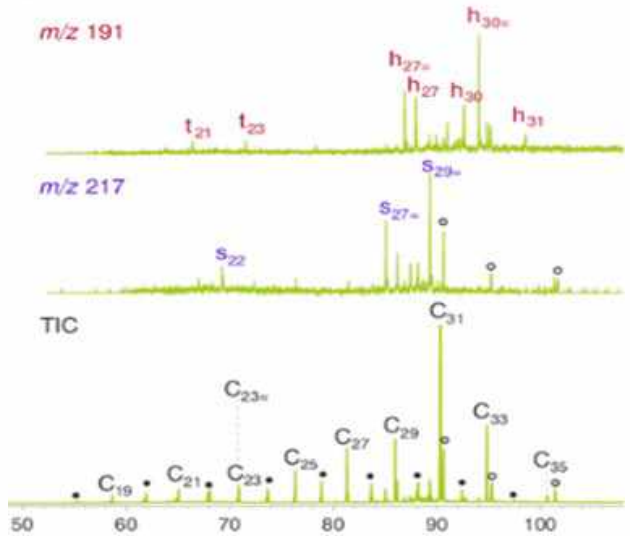


Environmental Forensics

- GC-FID
  - Common
  - Primarily used for hydrocarbons
  - Usually quick runs
  - Provides enough information to identify product type
  - Fine details and contamination of biogenics not easily determined



- GC-MS
  - Molecules are ionized and broken into fragments, which are then detected based on their mass-to-charge ratio
  - Useful for compound identification
  - Can determine presence of biogenic compounds, but requires training in interpretation and knowledge of important ions



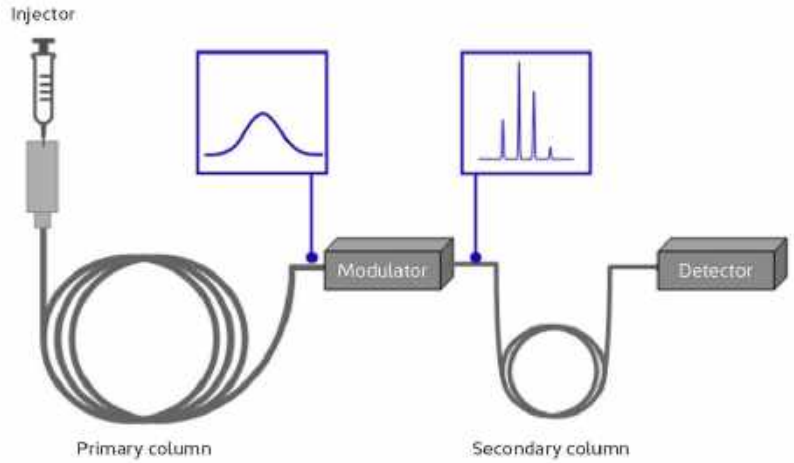
- 2D GC…

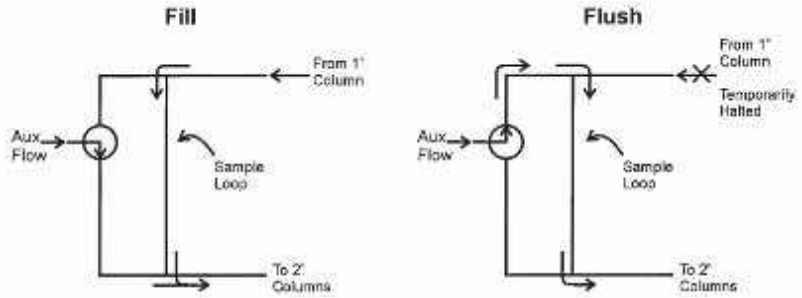
The Advantage of the 2D GC

VS

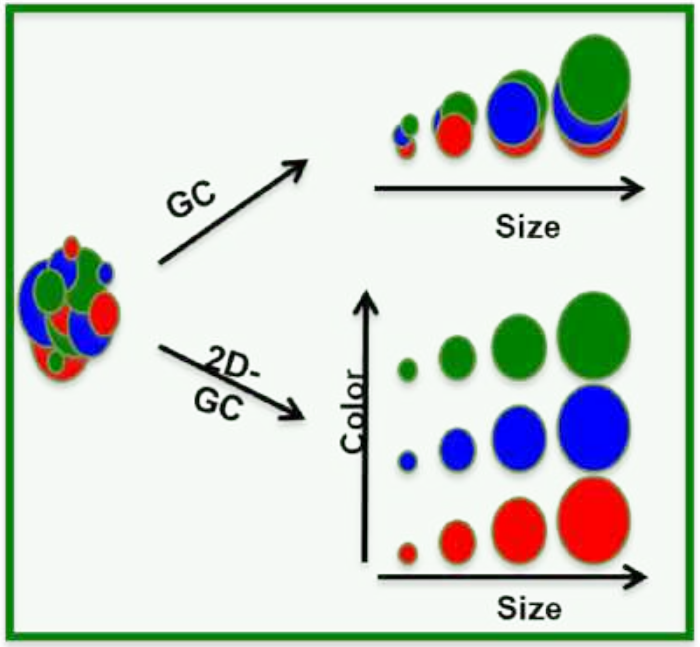
Principles

- 2 columns, one long, one short
- Modulator
- Gives rise to modulation cycle
- Types of modulators
  - Thermal modulators
  - Flow modulators





The Benefits of 2D GC



- Multi dimensional, x, y, z
- Better separation of co-eluting compounds and better specificity
- Less ambiguous interpretation
- Peak capacity
- Separates based on two properties
- Fuller picture – Better product and structure identification

2D GCs at AGAT

- 2D GC-FID
  - Used for broad range of compounds C6-C50 and PAHs
  - Primary instrument for biogenic vs petrogenic analysis

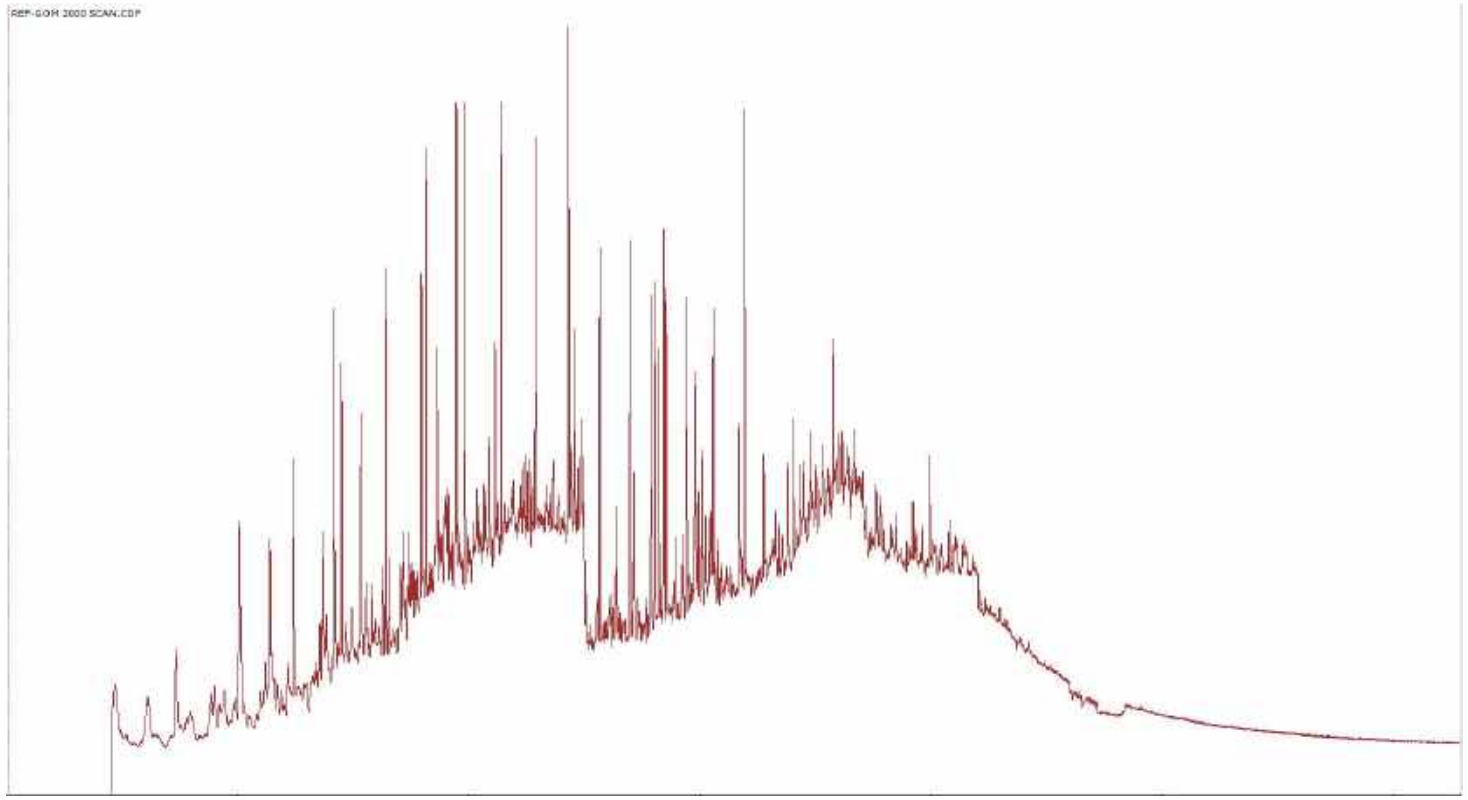
- 2D GC-TOF/MS
  - Also has FID detector
  - Used for light compounds, primarily condensates and light fuels
  - Range usually C5-C35
  - Primary instrument for compound fingerprinting (over 200 compounds mapped)

Uses

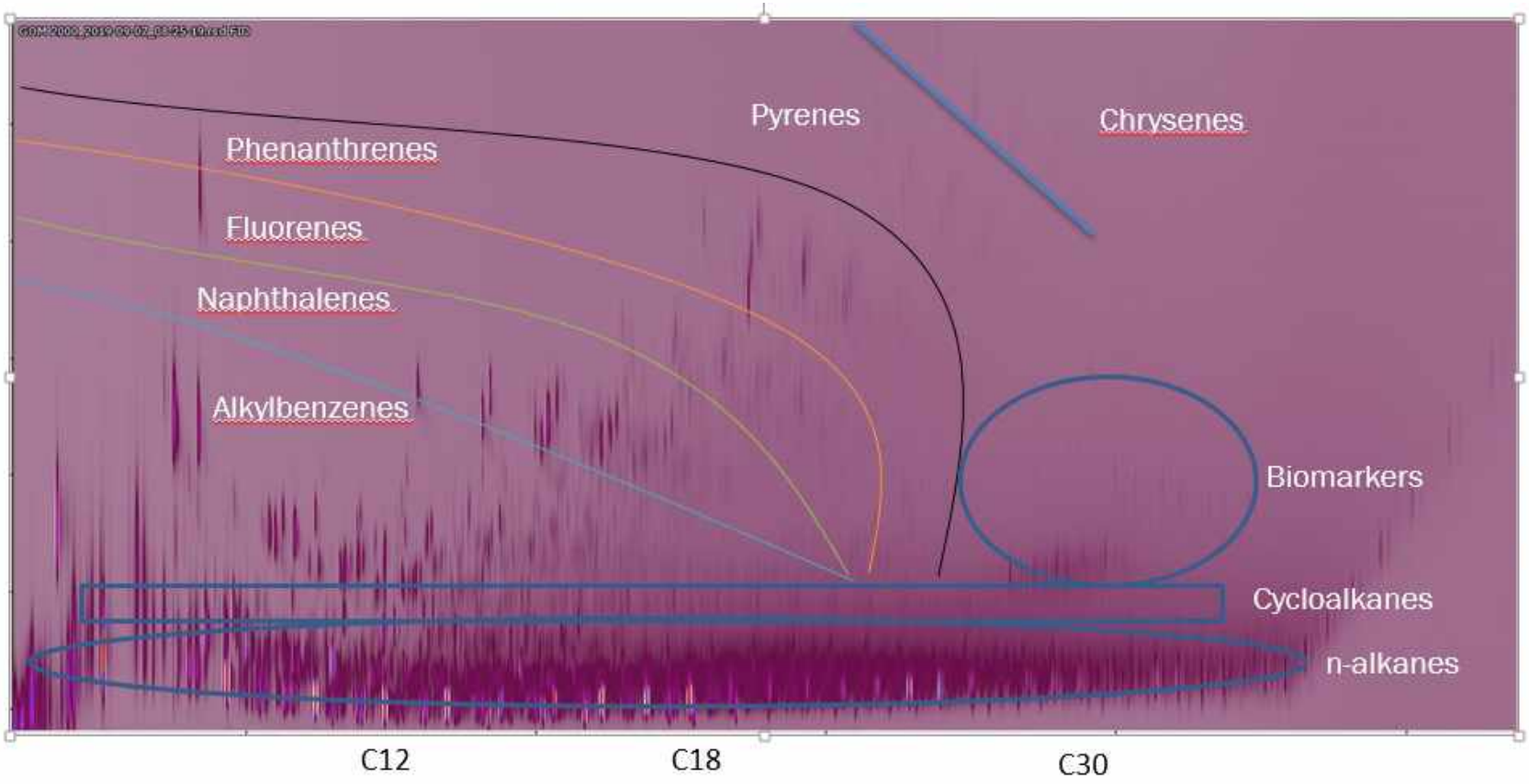
Currently offered

- Product identification and characterization
- Source identification and characterization
- Compound Fingerprinting
- Ecotoxicity
- F2-F4 Biogenic analysis

Old 1D Output

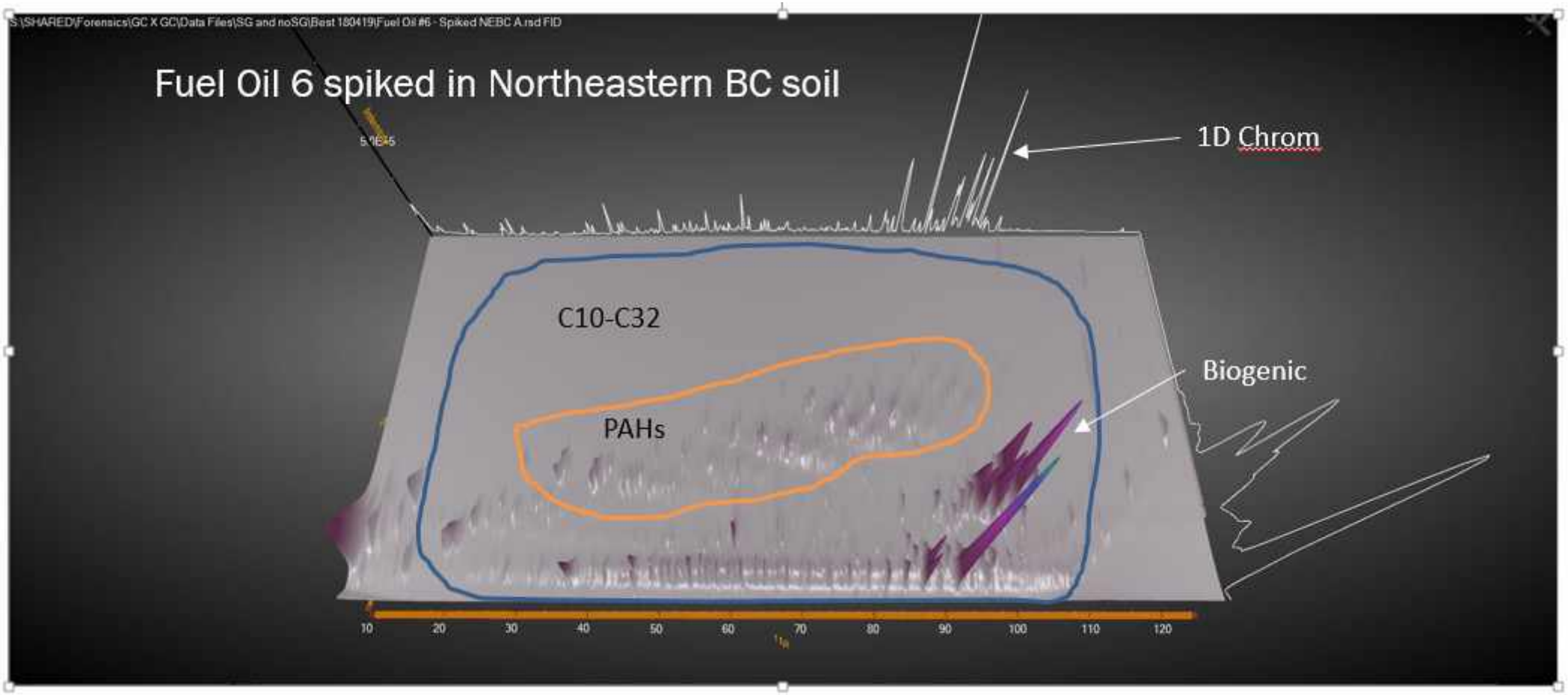


Chromspace 2D Output

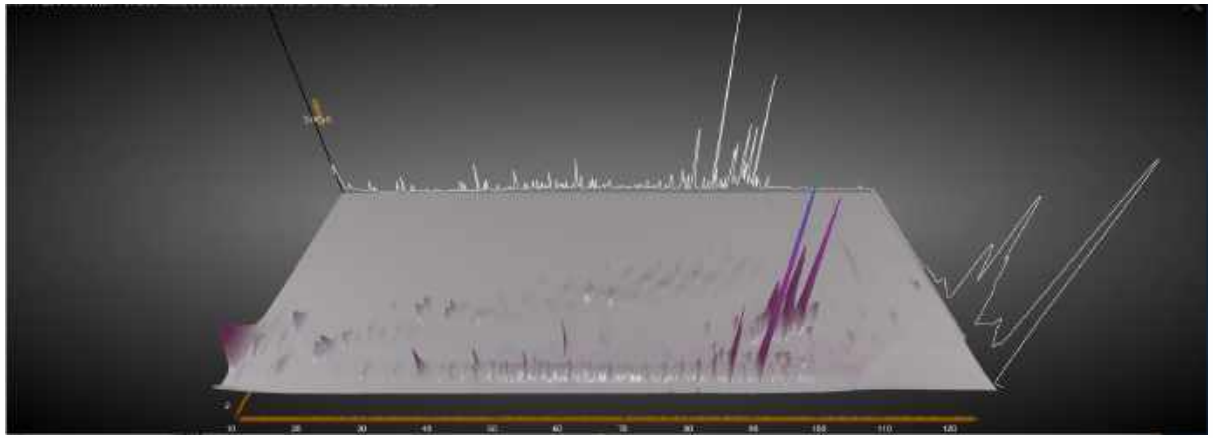


A Gulf of Mexico Standard oil, run using the 2D GC, with groups labelled. Included are mono and tri aromatic steranes, common biomarkers.

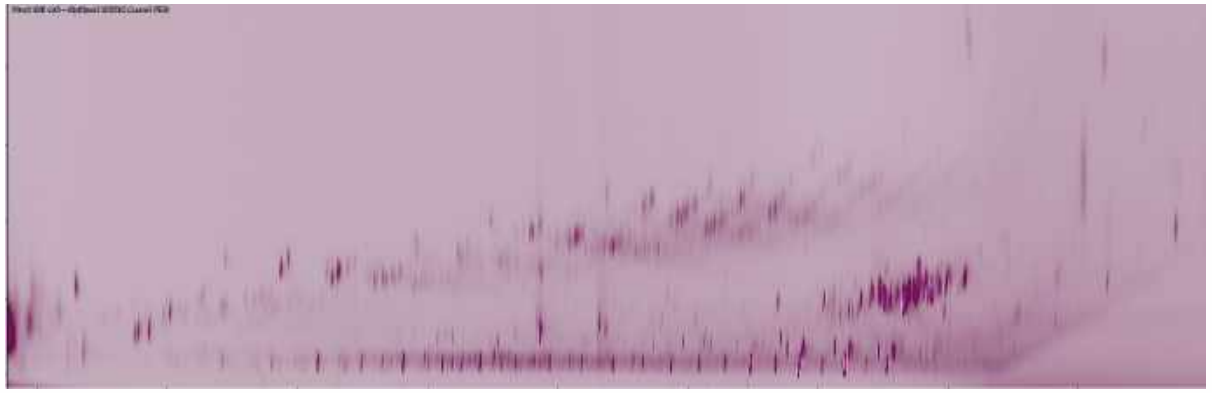
Chromspace 3D Output



Comparison 2D Vs 3D Output



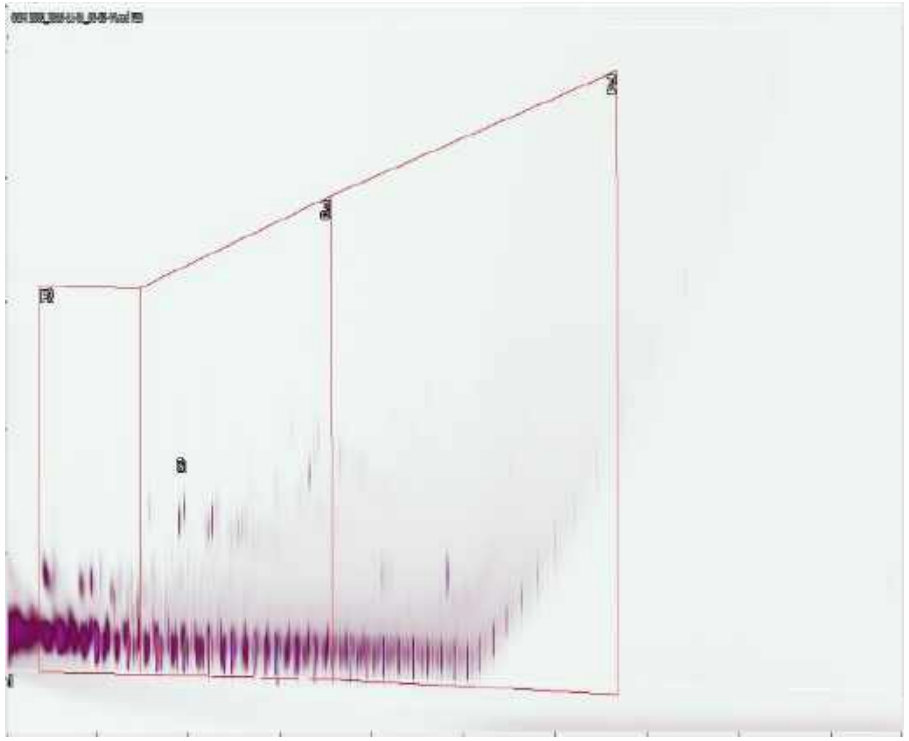
Can analyze with either 2D or 3D output.



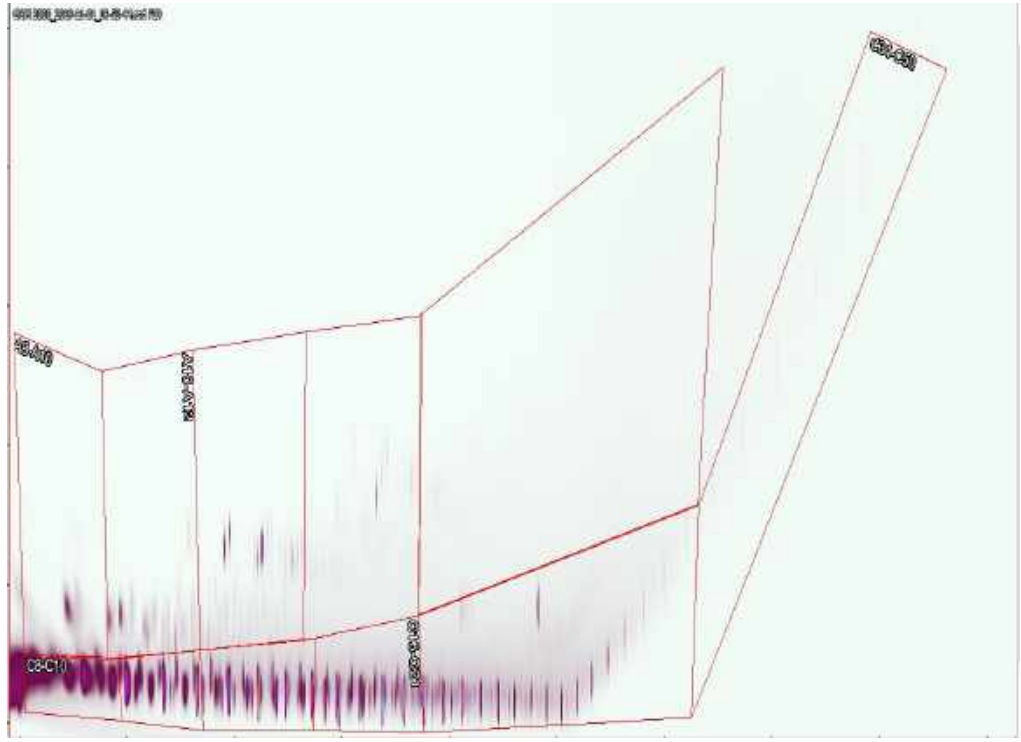
Can analyze by groupings (B, N, P, etc.) or by using individual compounds.

Stencils

- Can be drawn directly on chromatogram
- Can be used for any grouping of interest
- Can also be used for specific compounds if required

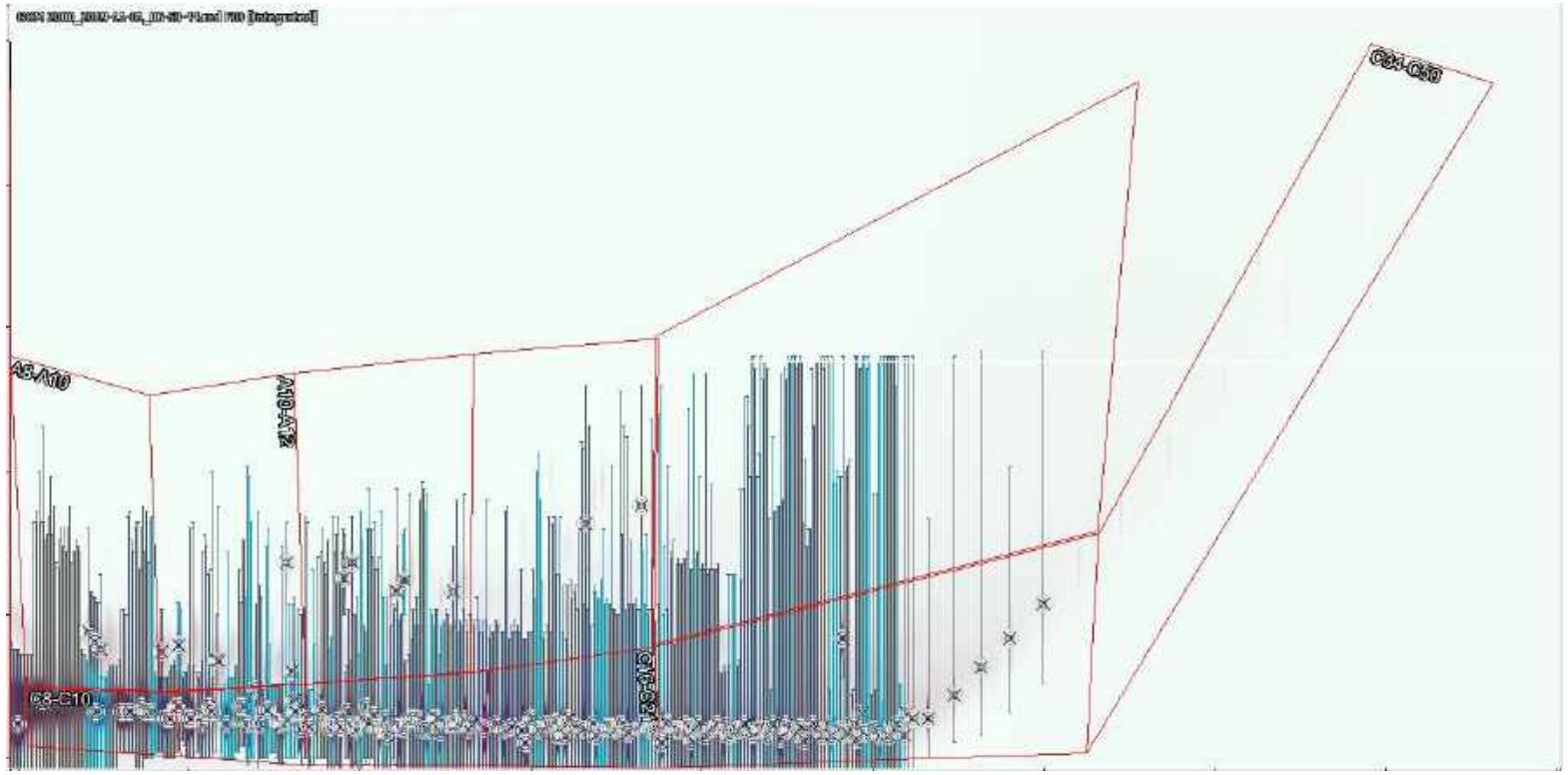


F2-F4 Stencil



Aliphatic/Aromatic stencil

Analysis



Biogenic Analysis

- Non-biogenic (petrogenic, anthropogenic)
  - Petroleum origin
  - Oil, Gasoline, diesel
- Biogenic
  - Naturally Occurring Hydrocarbons
  - Mostly F3, but some F4 compounds
- Can cause regulatory exceedances
  - TOC> 28% = F3 exceedance
  - TOC > 40% for Peat

Petrogenic vs Biogenic

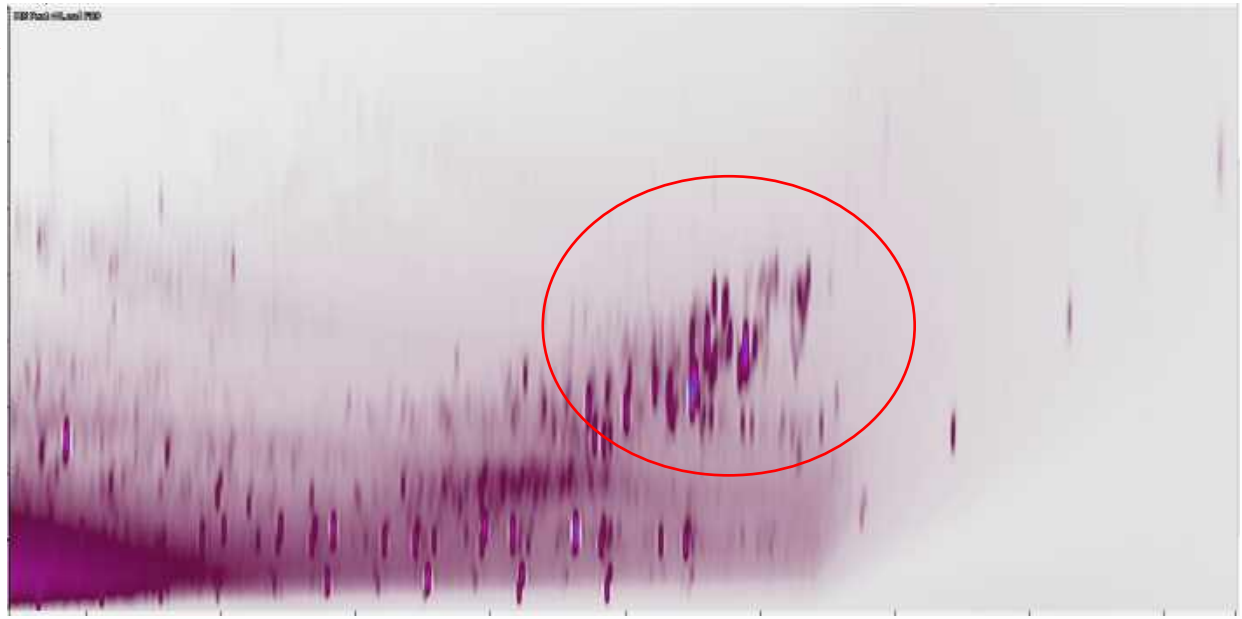
- Silica gel cleanup
  - Removes polar organic compounds, which biogenic compounds tend to be
- Background subtraction
  - Removes background interference from underlying environment
- Biomarker analysis
  - Look for specific compounds known to be biogenic
- BIC Scale analysis
  - Useful for determining false positives
- GCxGC Biogenic Analysis
  - New method to separate biogenic and petrogenic material and quantify them separately

Silica Gel Cleanup

- Useful for the removal of biogenic compounds if a clean sample is required
- However, it is not selective for only biogenic compounds
- Silica gel removes polar compounds from a sample
    - As most biogenic compounds are polar, very useful.
    - Can also remove some petrogenic compounds if they are sufficiently polar, ie: alcohols, acids and esters.
    - Can leave behind non-polar biogenic compounds, such as certain plant waxes.

Silica Gel Example

Polarity increases



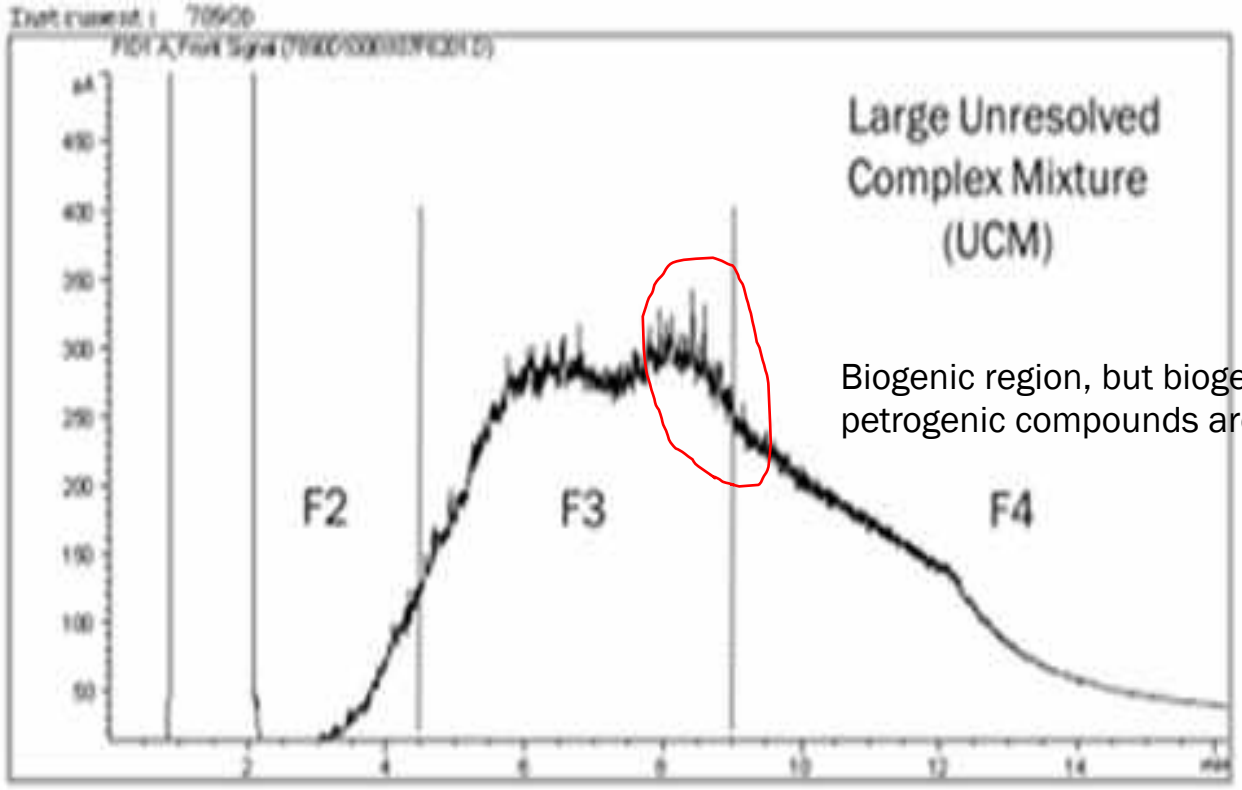
Before

After

1D Output

- Chromatogram features not well defined
- Not easily quantifiable
- Need MS to determine specific compounds
- Looks like…

1D Output

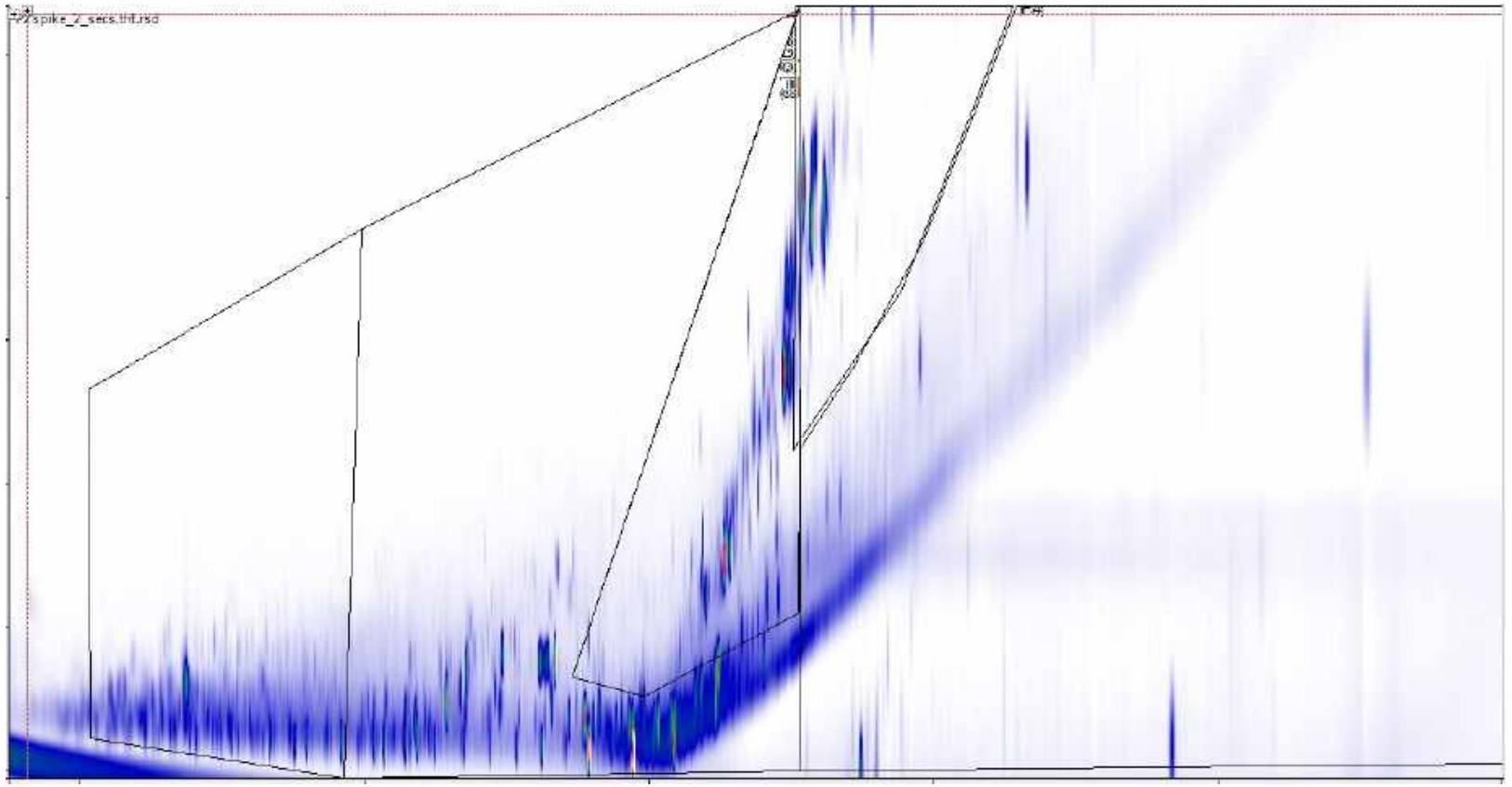


Biogenic region, but biogenic and petrogenic compounds are mixed

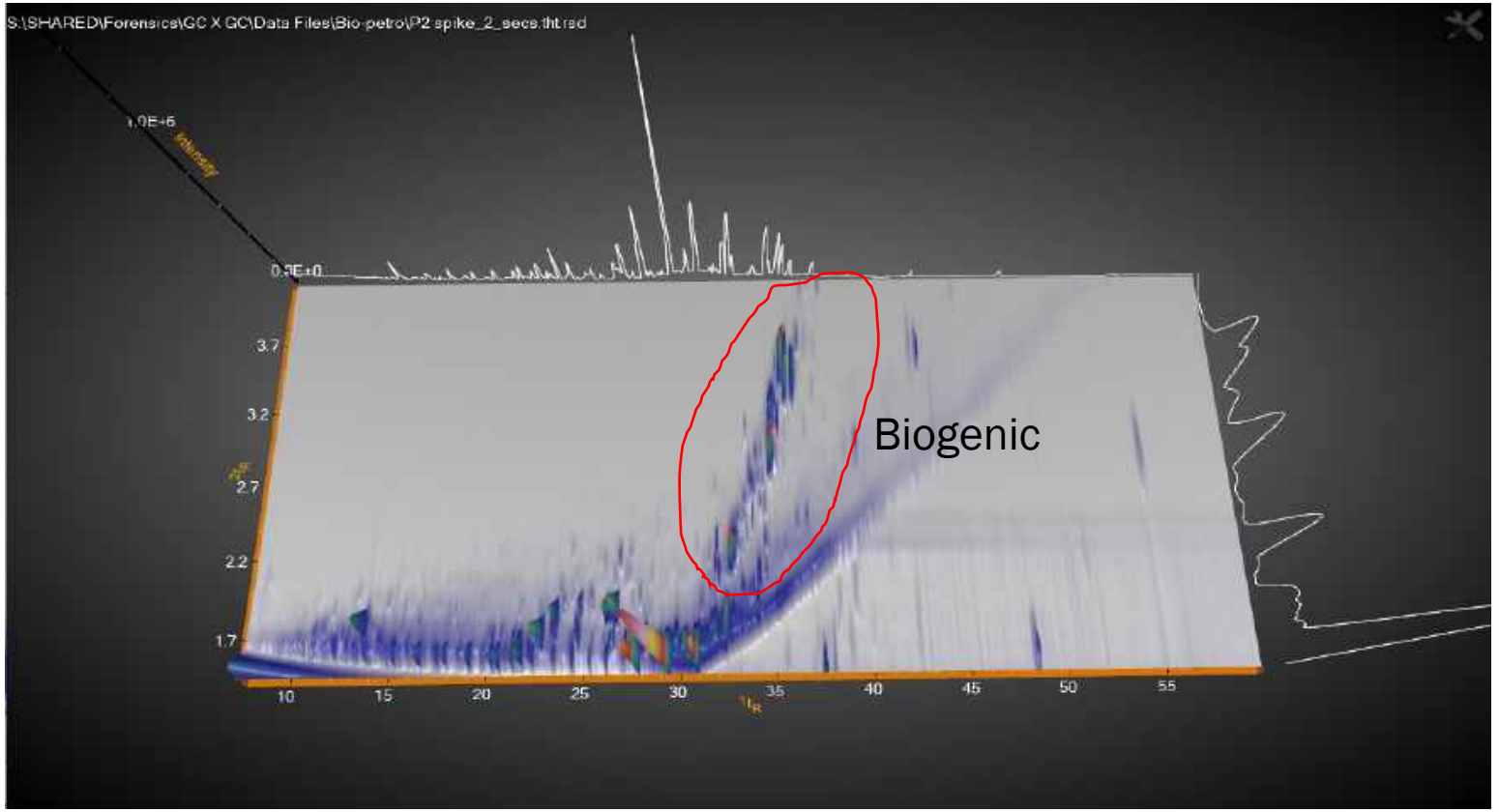
GCxGC Biogenic Analysis

- Using stencils, the method is able to partition off different regions of the sample as petrogenic or biogenic
- Once a stencil has been applied, data is integrated and report generated with areas for each region.
- Results can either be reported in percent of total (area percent) or as concentration
- Fully validated in soil for CCME PHC Method

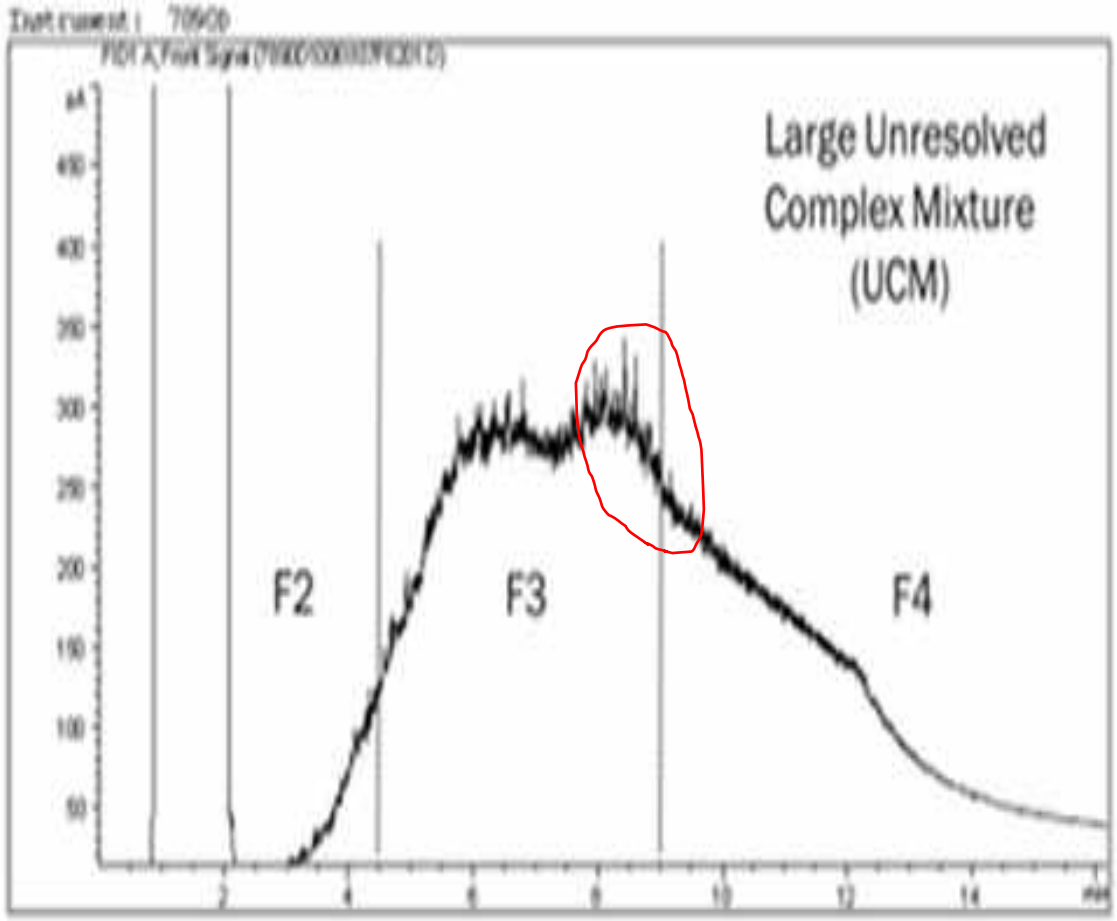
GCxGC Biogenic Analysis

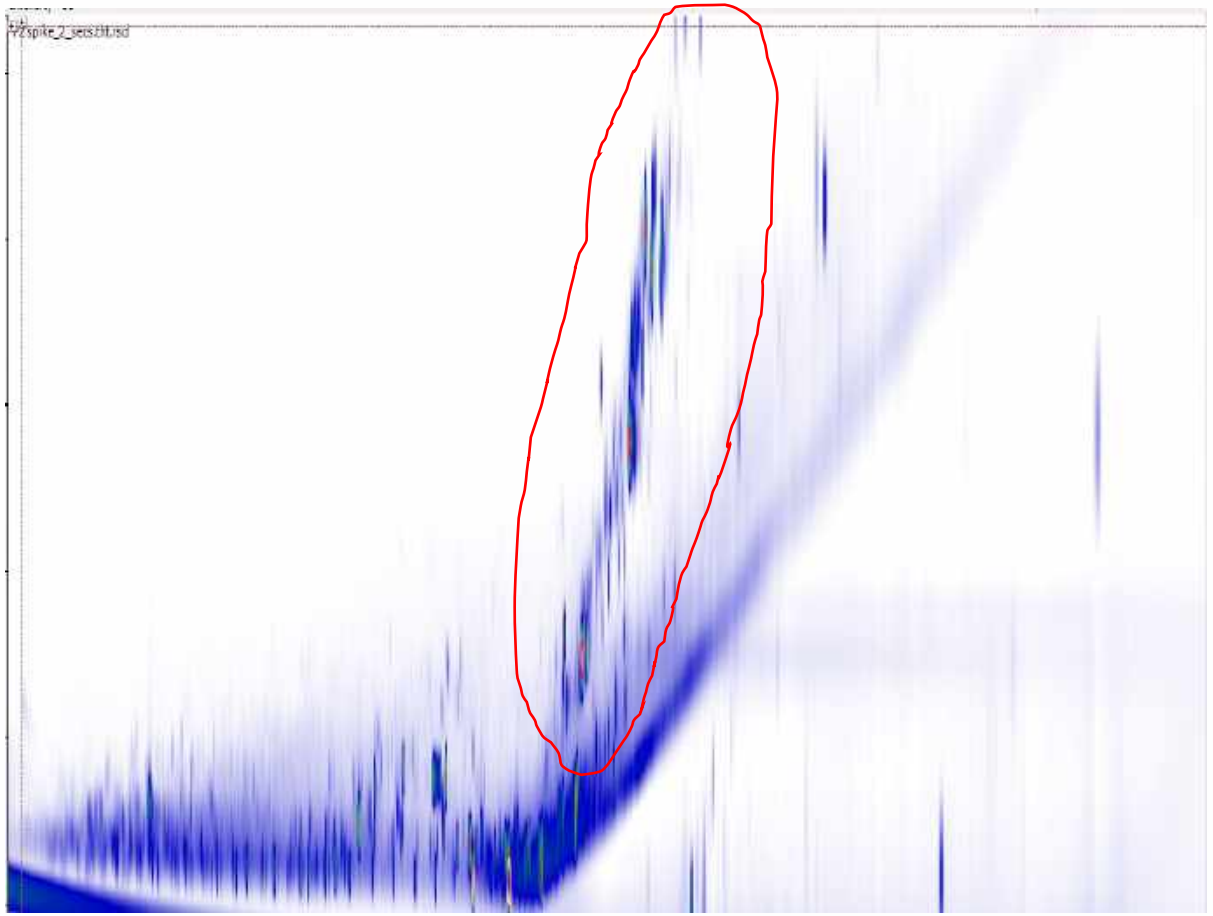


New Biogenic Analysis



1D Vs 2D





Benefits

- Quick
- Software can handle intense integrations required
- Software is intuitive/user friendly
- 3D plotting makes explanations to clients simpler
- Minimal overlap between the regions; less than 10%
- Any sample above guidelines can be analyzed

Biogenic VS BIC

Biogenic

- Works for all product types including heavy fuels
- Applicable regardless of moisture content
- No direct calculations
- Some overlap between areas
- No conditions for use
- Quantitative
- Can be extended to use in other matrices

BIC

- Limited to mid range fuels, not applicable to heavier hydrocarbon products
- Not to be used for high moisture samples
- Calculations required
- No noted overlap
- Strict conditions must be meet before application
- Semi-quantitative
- Only applicable to soil samples

GCxGC Method Performance Data

% Recoveries for high organic content peat soil spiked with heavy oil

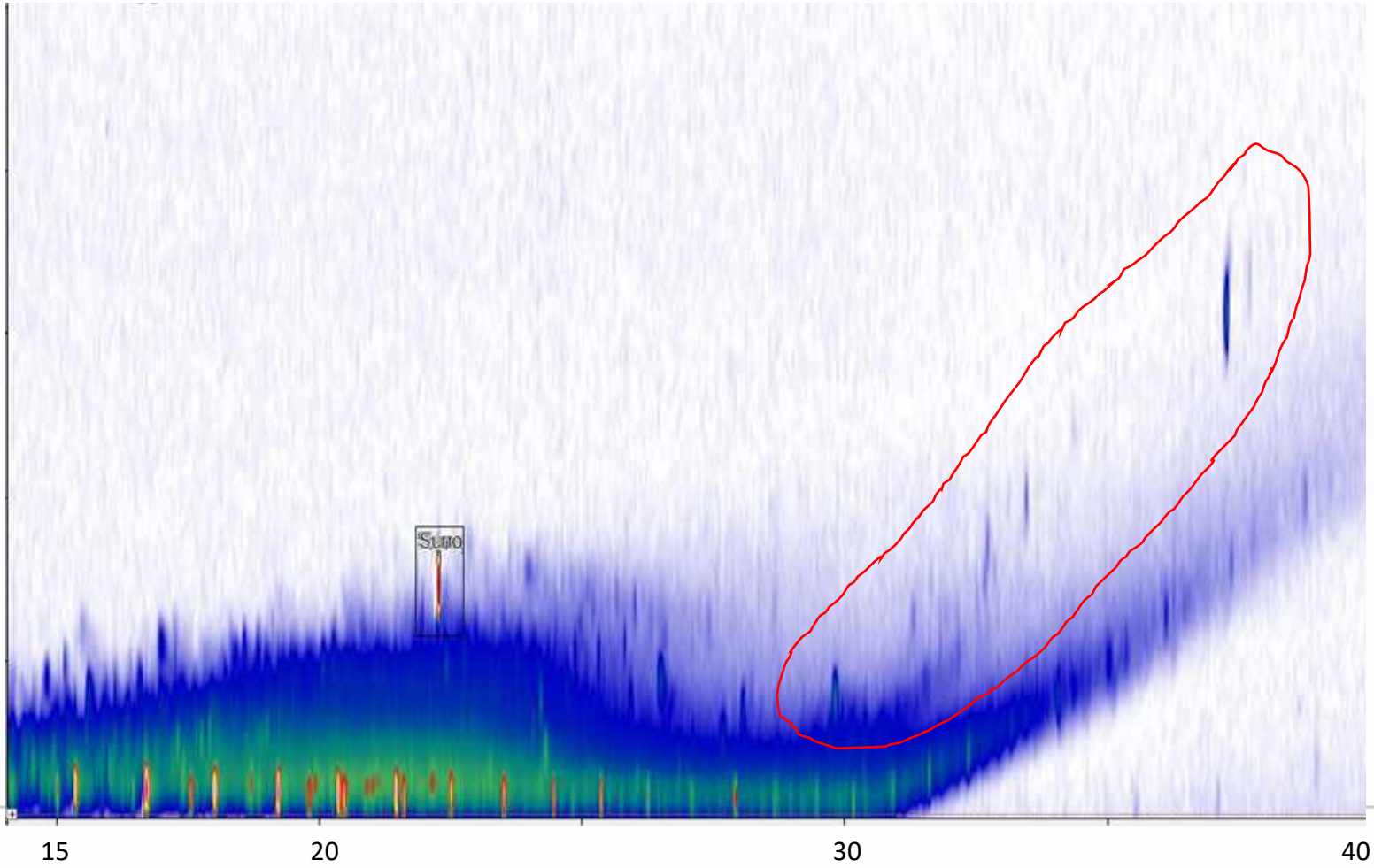
	Recovery (%)	
	Low/mid level spike	High level spike
F2	102	103
F3	103	101
F4	108	96
F3a	99	99
F3b	104	100

Initial testing is positive indicating the biogenic/petrogenic contributions can be separated/differentiated

Project Examples

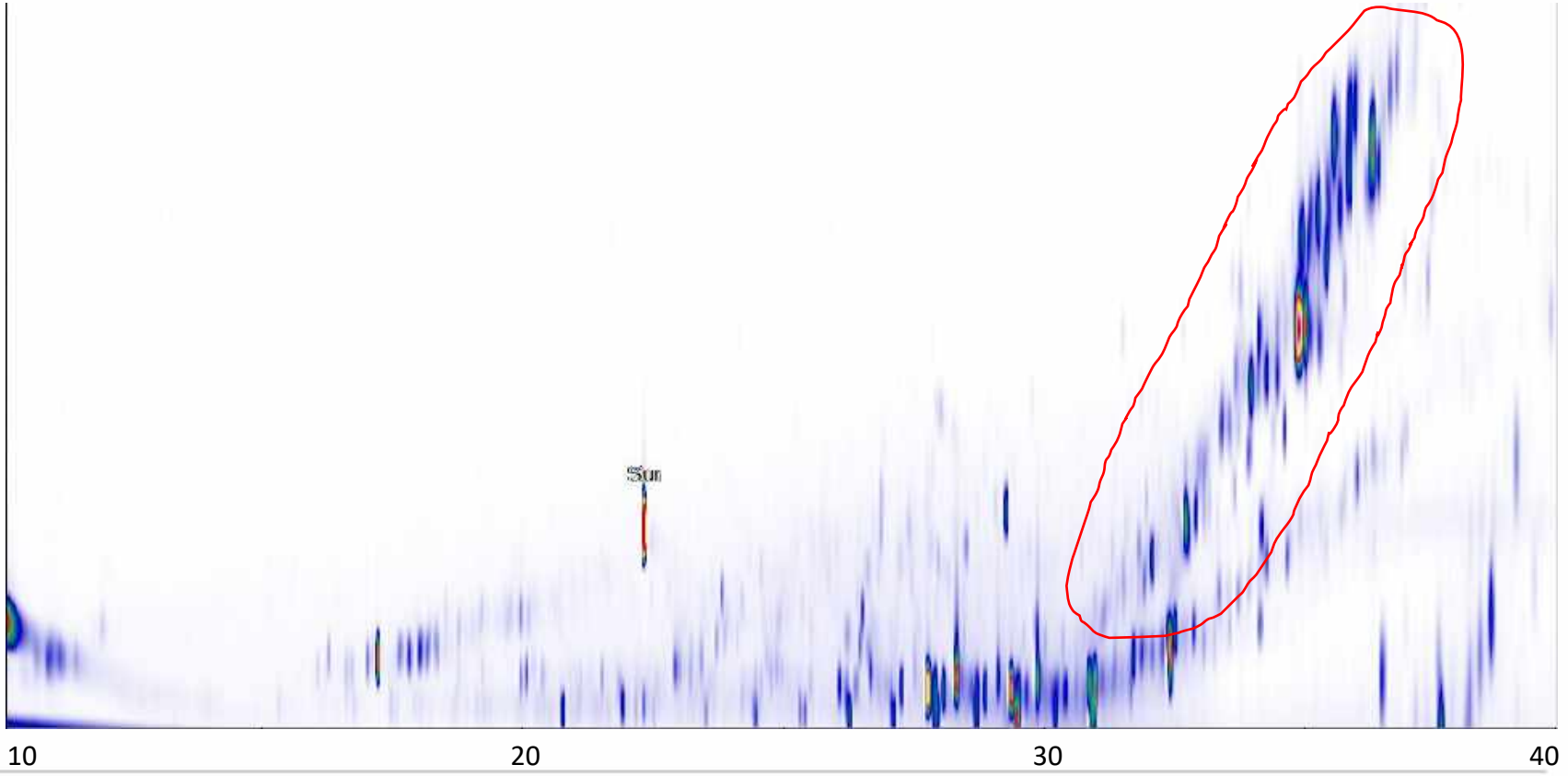
Example 1: Low biogenic content

- Waste sample
- Wanted to know percentage biogenic for disposal purposes
- Around 1.5% biogenic
- Disposal of petrogenic material still required



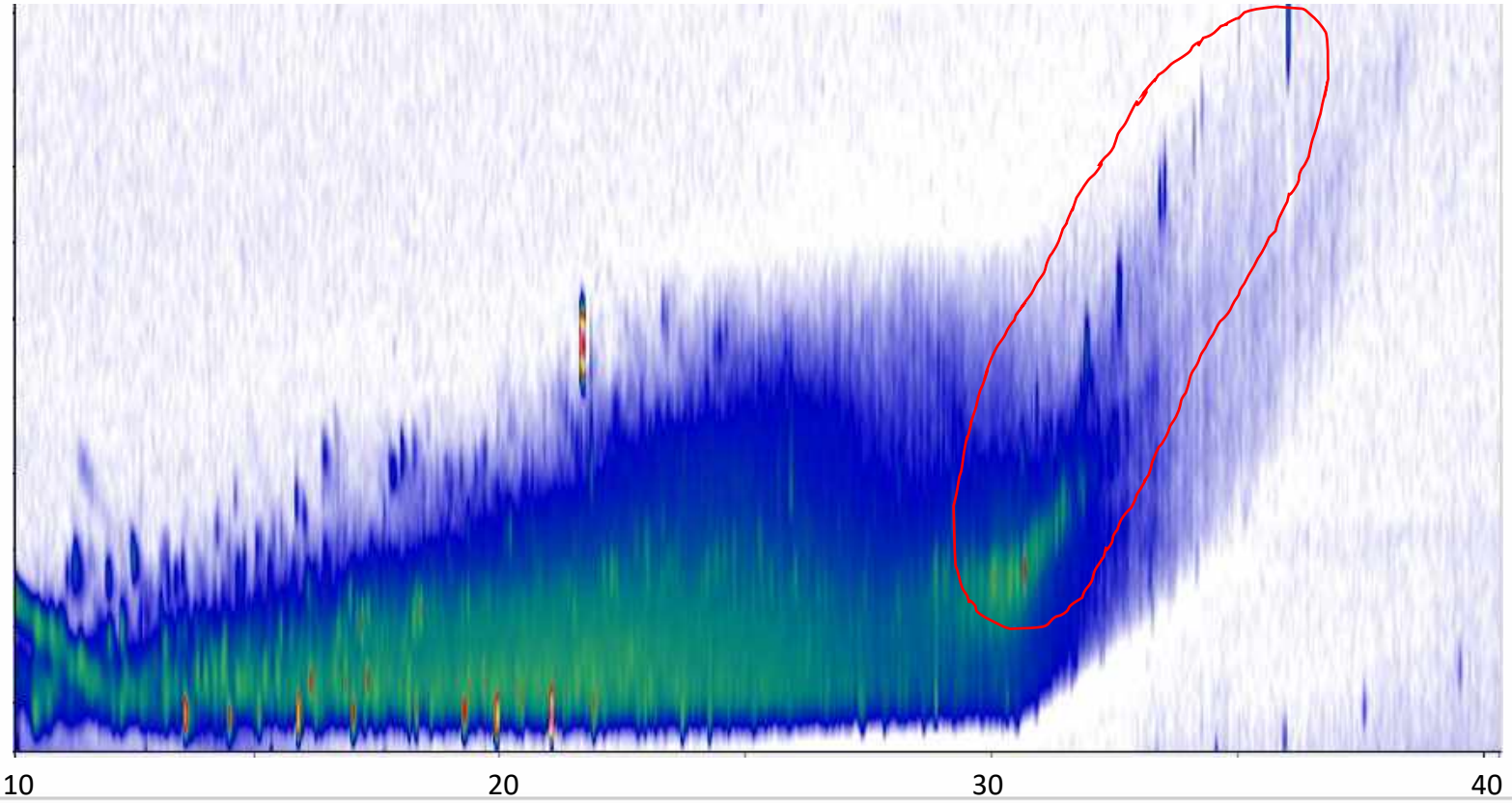
Example 2: High biogenic content

- Sediment sample
- Previous analysis showed high response in F3-F4 regions
- Wanted to know true nature of sample
- >90% biogenic
- Reduced concentrations in F3-F4 regions below guidelines



Example 3: Mixed biogenic and petrogenic content

- Soil sample
- Previous analysis showed high response in F3-F4 regions
- Wanted to know true nature of sample
- 15% biogenic
- Remediation of petrogenic material still required



Why this method?

- Cut costs on remediation
- Can be used in legal cases where disputes over impacts occur
- Reduces human errors in estimating biogenic content
- No restrictions on sample type or makeup
- Can be used for any kind of petroleum contamination.

Future Work

- Extend this method to more difficult contaminant types and matrix types
- Compare method directly quantitatively to BIC and other approaches
- Validate method in other matrices that arise
- AGAT is proceeding with accreditation, but as written in the CCME guidelines: “alternate methods may be acceptable where there is a supporting rationale for such methods,” and clients have successfully submitted our results to get closure or approved risk management plans.

Questions?

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