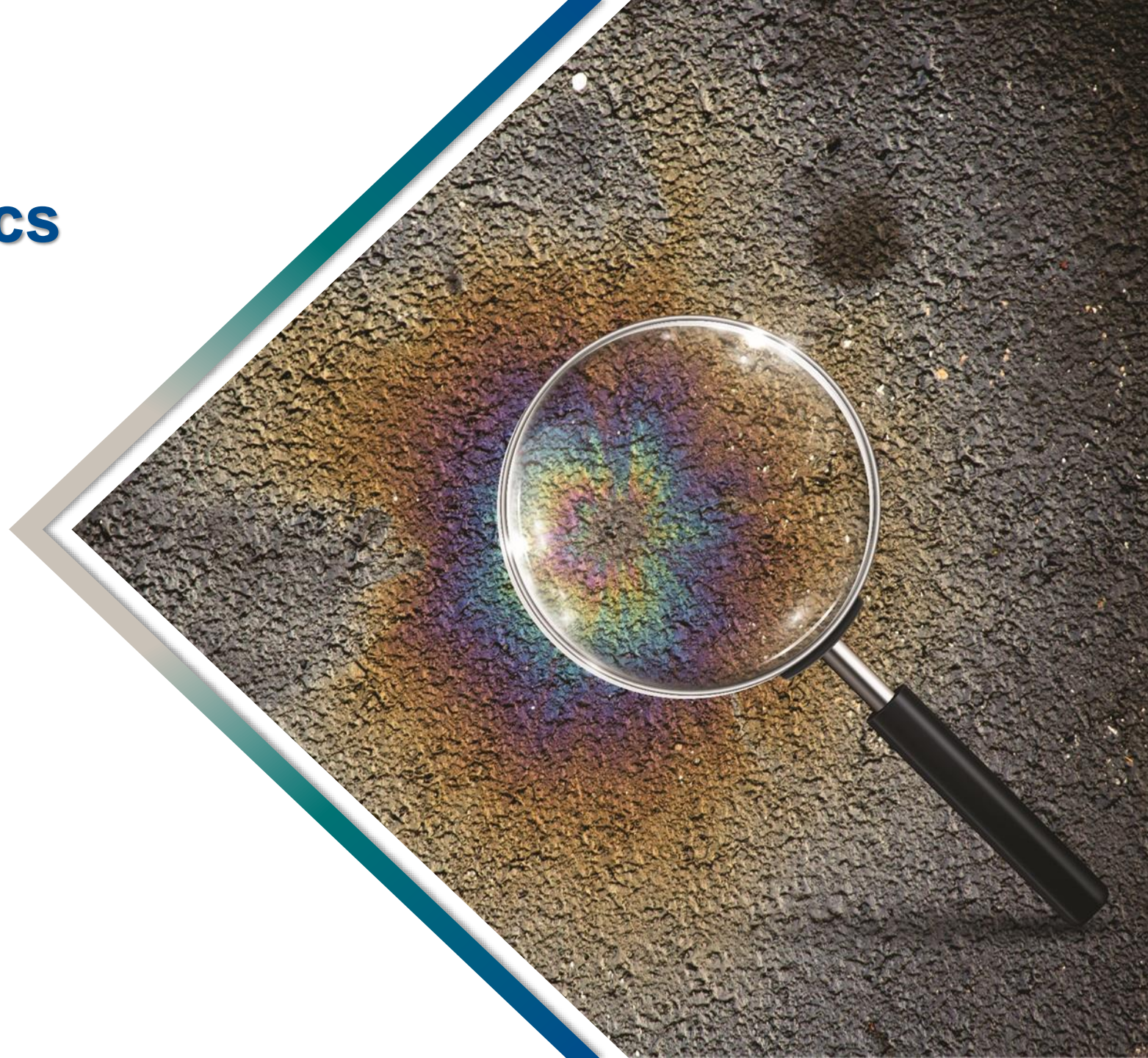


The Case for Hydrocarbon Forensics

National Environmental
Monitoring Conference
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CEAC

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Agenda

Strategies

- Define the question, evaluate existing information, , know the site history, evaluate data quality, identify lines of evidence

Methods and Data Types

- Historical, hydrological, chemical, isotopic, Tiers

Applications/Case Studies

Questions

Forensic Evaluations

Strategies

- Define the question, DQOs and MQOs

Types and Quantity of Data

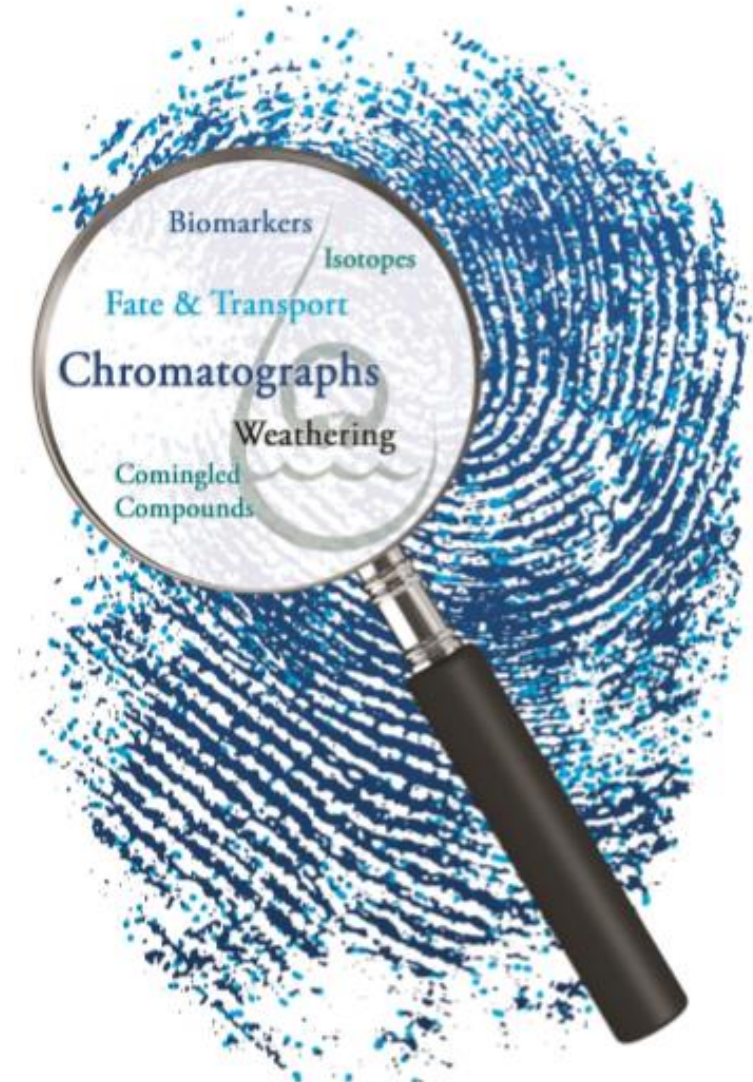
- Hydrological, chemical, isotopic
- Tiers

Data Analysis

- Completeness check, formal or focused validation, data conditioning and framing

Communication

- Making the case, graphics and simplification, data presentation



Strategies

- Define the Question/Objectives
 - Type of Hydrocarbon (HC).
 - Source of HC or chemical of interest (Cr, As, Hg ...).
 - Regulatory Limit Comparison vs Fingerprinting Forensics.
- Develop DQOs (a process), and MQOs.
- Identify Analytical Approach
 - Historic (secondary) Data.
 - New Data – Tiers and tradeoffs.
- Develop Lines of Evidence
 - Does site hydrogeology fit with analytical data?
 - Do multiple chemical measurements converge or not.

Lines of Evidence that Converge

- Historical Background
- Historical Data
- Source Product(s) Data
- New/Planned Data based on DQOs
 - Specialized analytical laboratory, method & deliverables
- Information = reduction of data uncertainty.



Analytical Tiers

- Tier I – GC/FID. Whole Oil Analysis, Refined and unrefined components.
- Tier II – GC/MS (SHCs, PAH/APAHs, Biomarkers, PIANO).
- Tier III – CSIA (Carbon-stable Isotope Analysis).

- Other parameters ... metals, sulfur, organic Pb, Mn, *etc.*

START WITH LOWER TIERS FIRST AND WORK TOWARD HIGHER TIERS

Example 1 – ID Type of Hydrocarbon Spill

- Site Information
 - Gathering system for oil and refined petroleum products.
- Source Types
 - Oil material from near location.
 - LNAPL from Monitoring Wells (match to oil?).
- Analyses – Compare Spills to Potential Sources
 - 8015M for Whole Oil Analysis.
 - Specific Gravity.
 - PIANO.
- Standards to match objective and background information
 - Gasoline.
 - Diesel.

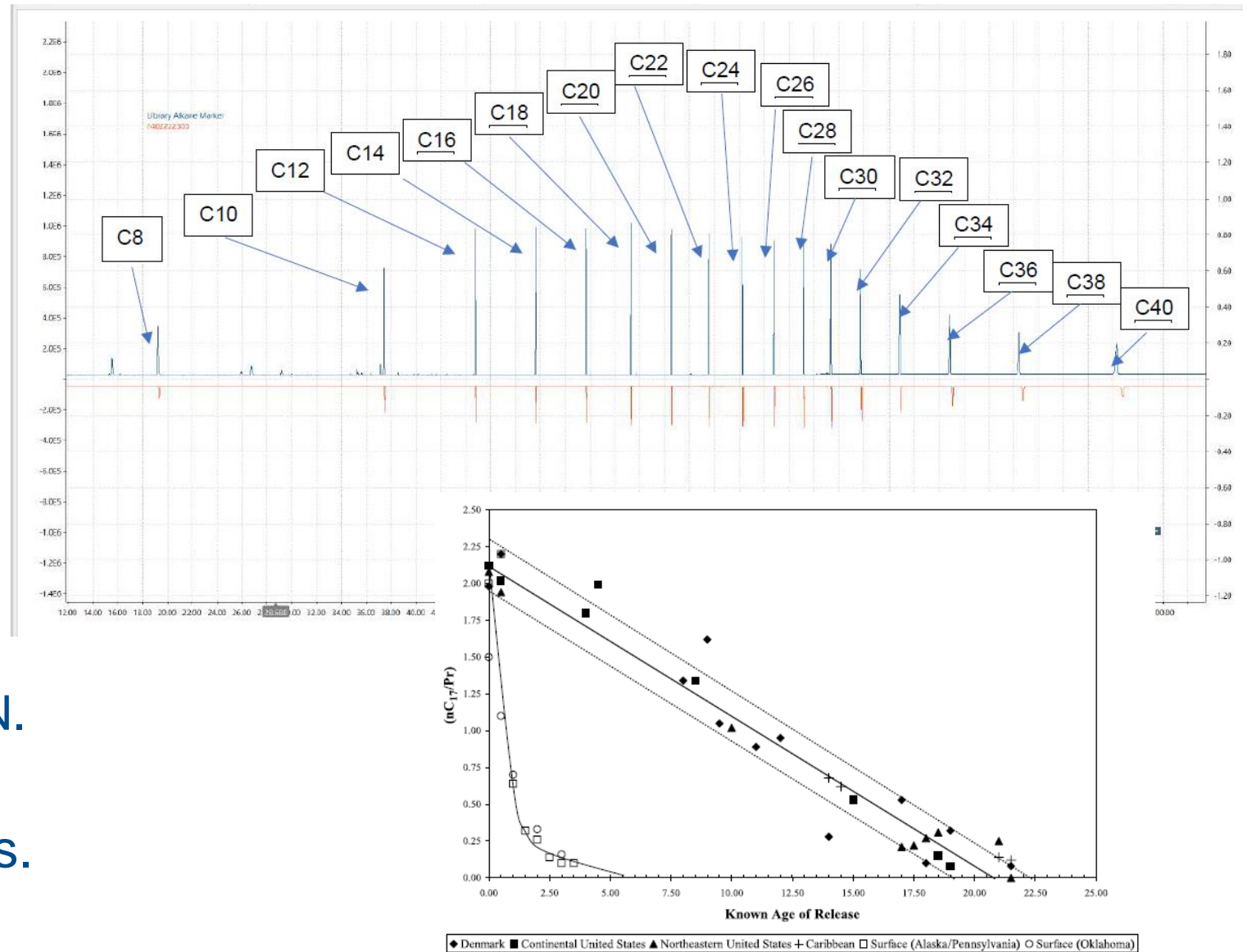
Data Visualization and Reduction

- Proprietary configuration of OpenChrom® software with MS library.
 - Produce chromatograms, enhance views, mirror overlays.
 - Process for PIANO analysis (~120 components).



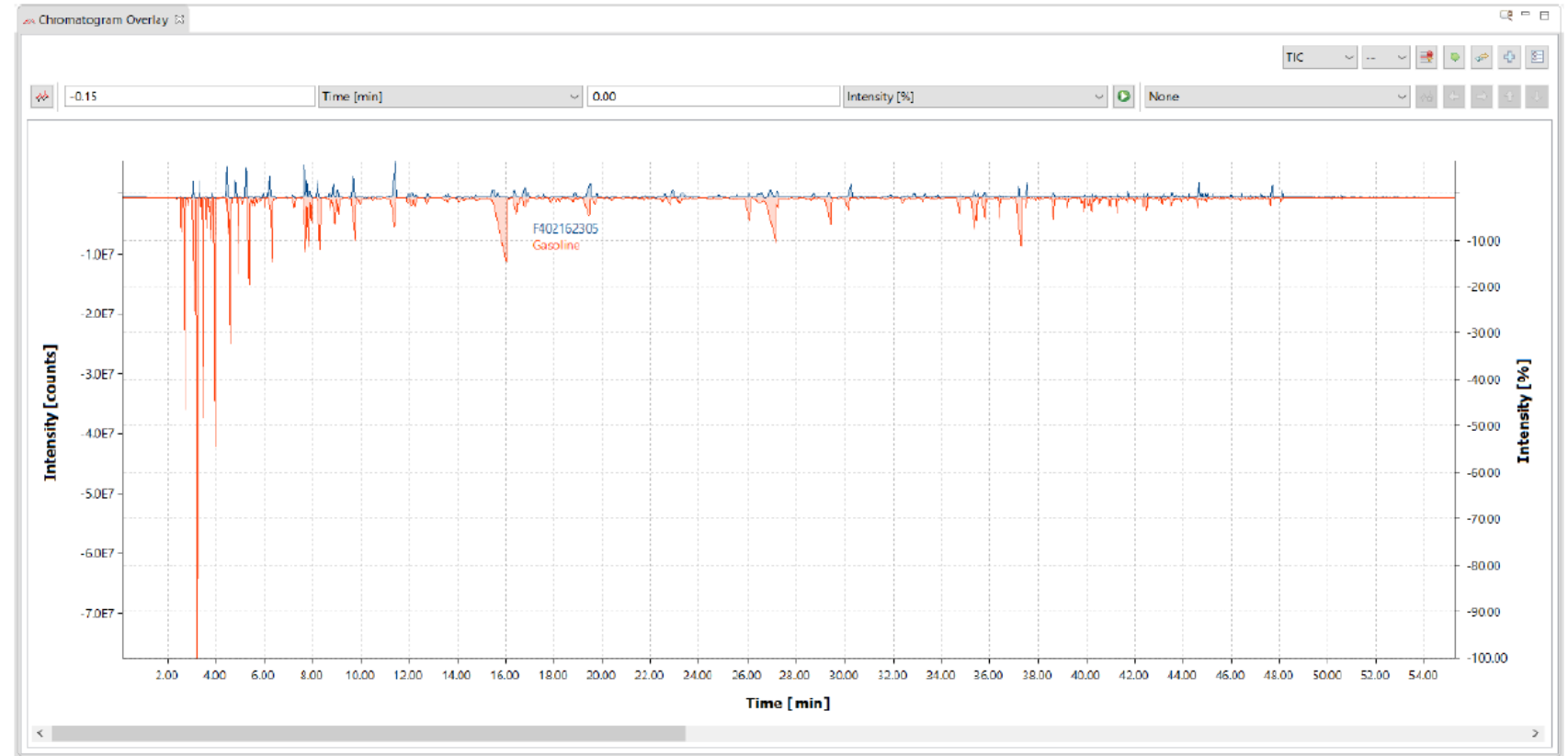
Data Analysis

- Data Quality Review
 - Method and field QC.
 - Blanks to sample ratios.
 - Surrogate recoveries.
 - Fingerprint features evident.
 - Peak symmetry, resolution, alkane/isoprenoids, S/N.
 - Consistent retention times across all analyses.



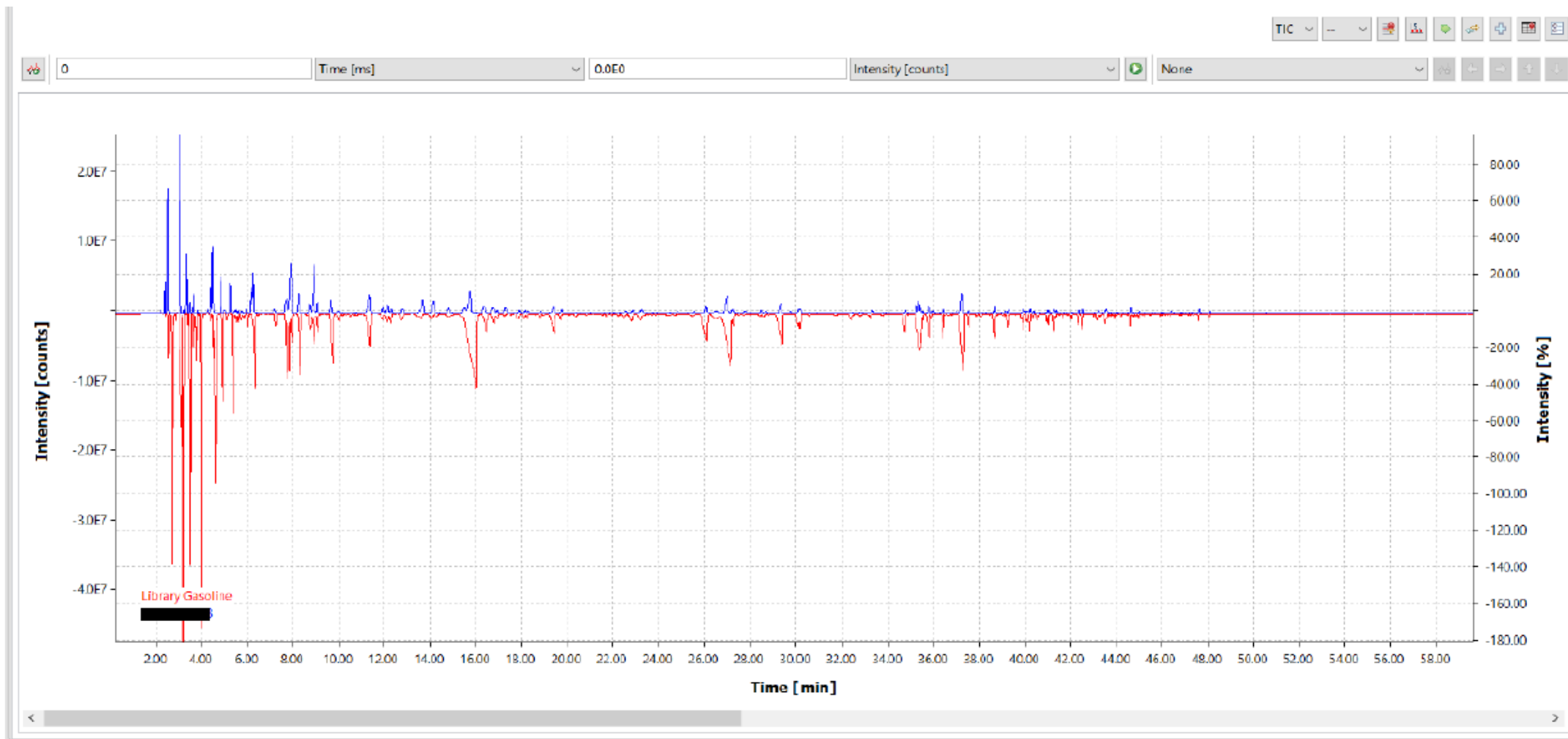
Whole Oil Interpretation C4-C44

- Mirror overlay
 - Laboratories Gasoline Standard to Samples AND prior Standard

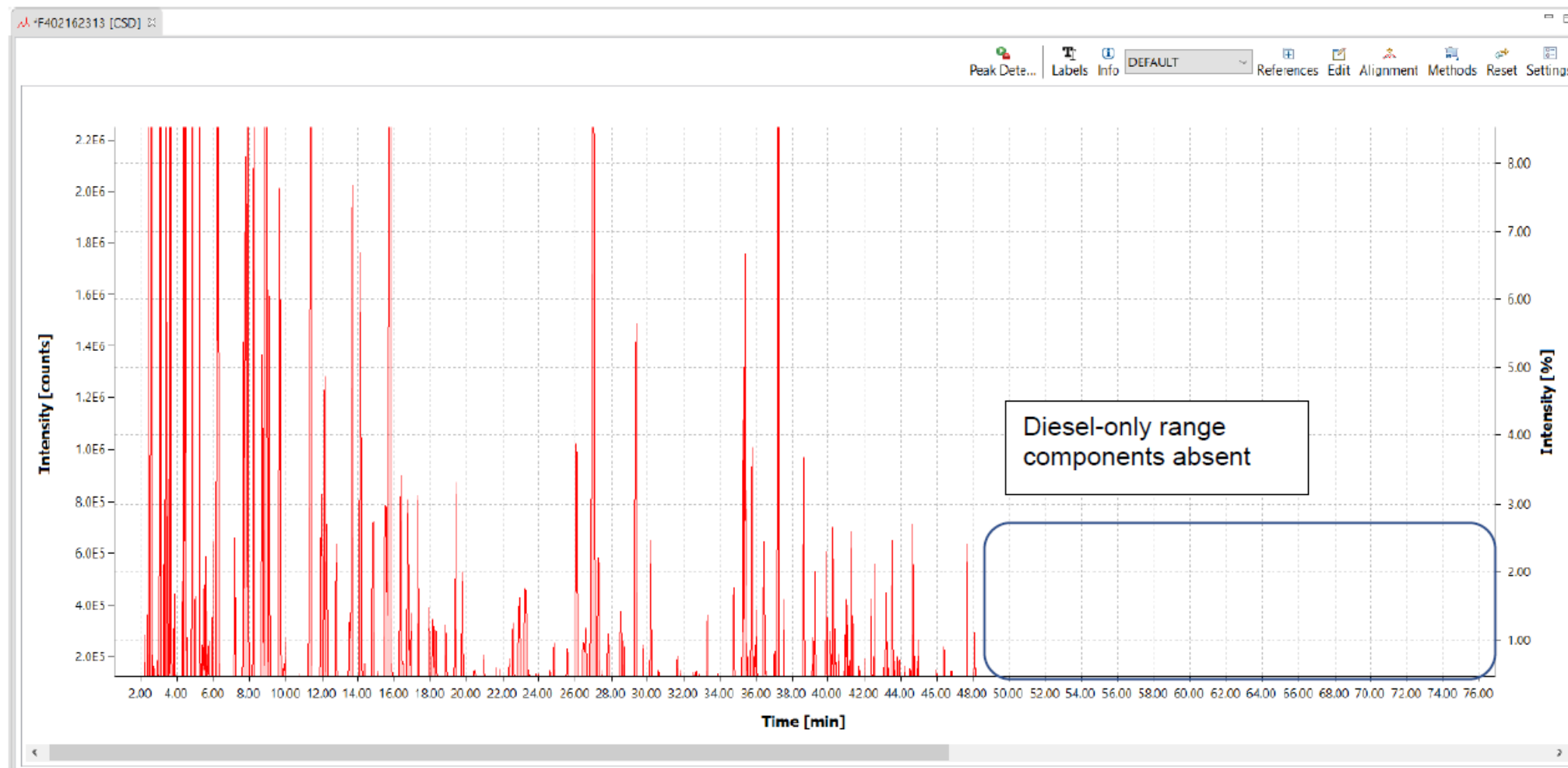


Reference standard indicated evidence of weathering, significantly reduced volatile components
Compared samples against recently obtained gasoline standard

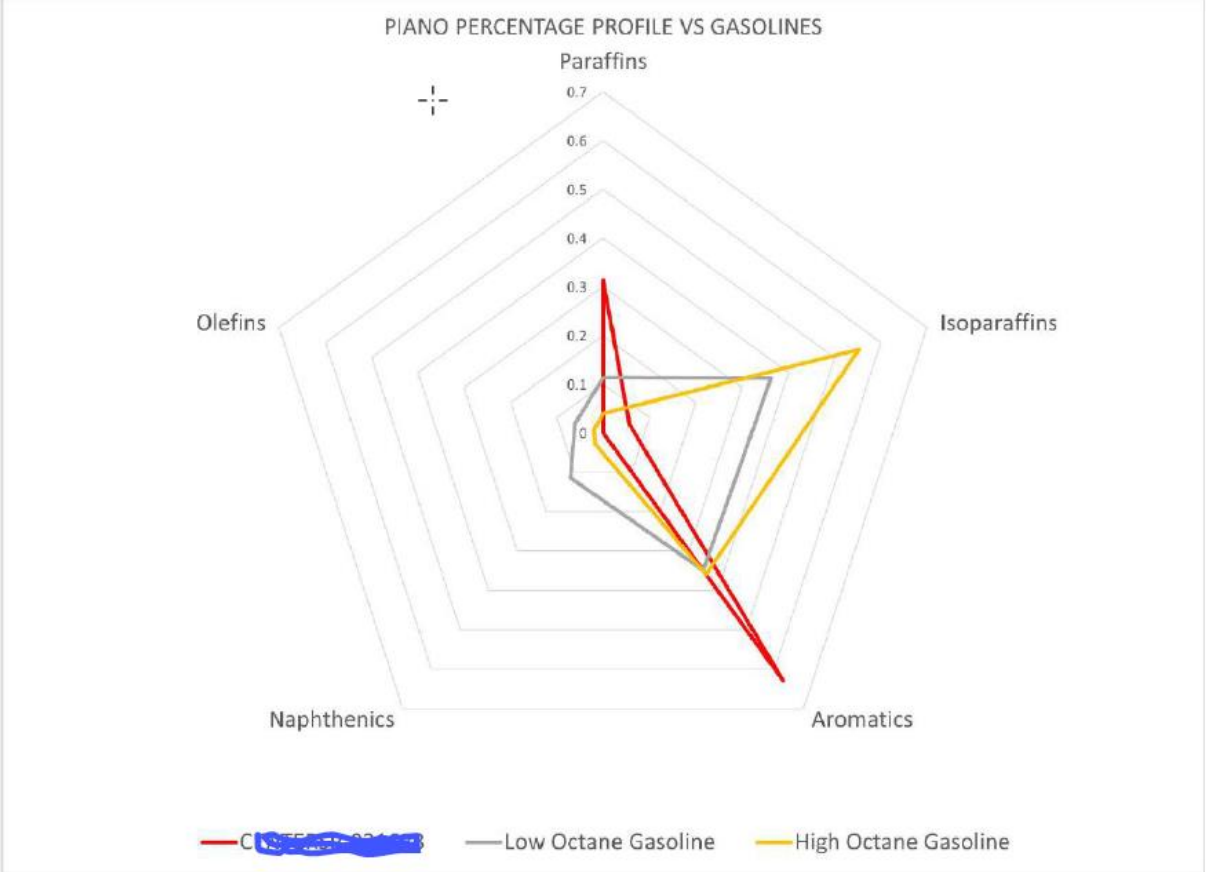
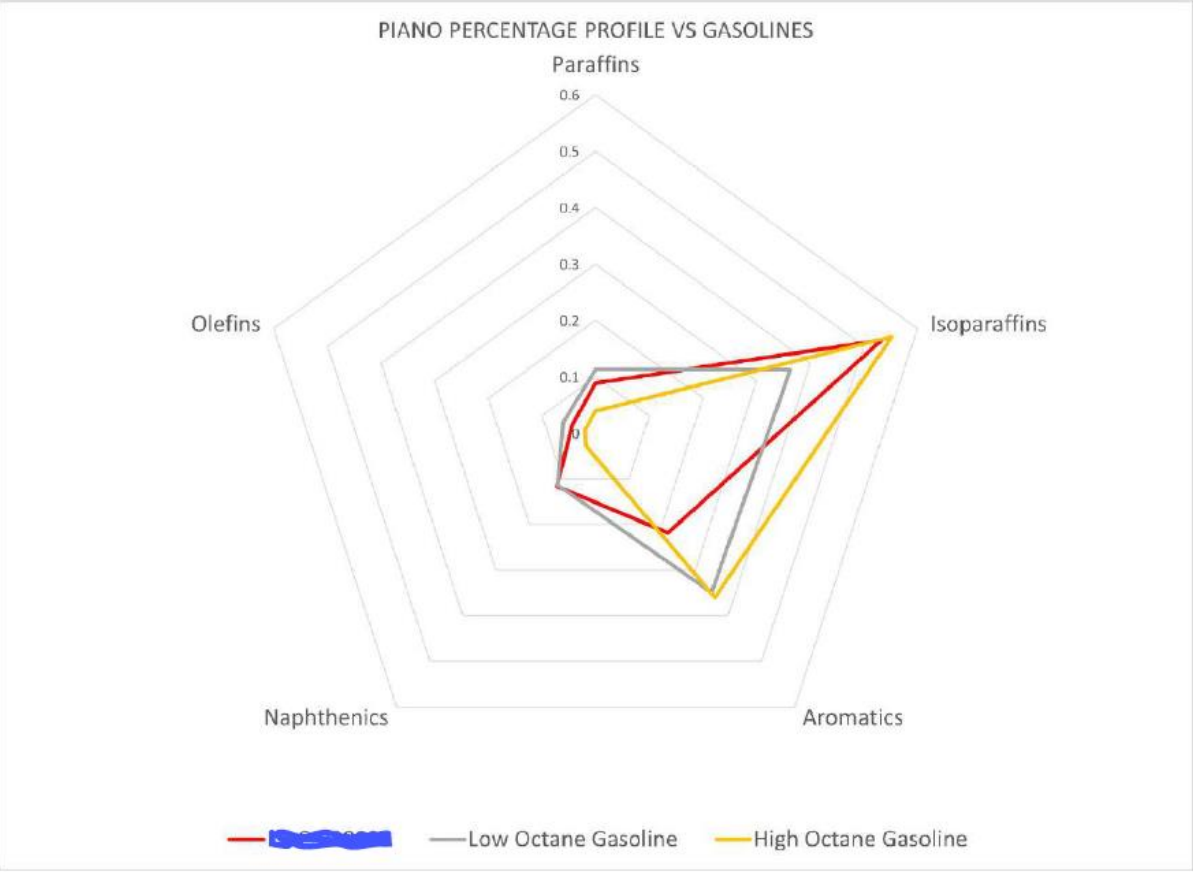
Sample vs Standard



HC Type Comparison



PIANO Analysis



Example 2 – ID Product Types, Mixtures, Degradation

- Site Information: Petroleum Refinery Site
 - ID product types for LNAPLs across facility.
- Source Types
 - Product reference samples from site laboratory.
 - Forensic laboratory reference standards.
- Analyses
 - Tiers focused on types, mixture information, level of degradation.
 - Tier 1: 8015M for Whole Oil analysis – GC/FID, ED-XRFS for sulfur.
 - Tier 2: GC/MS for PIANO compounds, GC/MS for alkyl-substituted lead compounds if exhibited gasoline characteristics.

Tier 1 – US EPA SW-846 8015M Whole Oil Analysis

- Qualitative only, used to determine carbon ranges and resolution, general areas indicative of refined petroleum types.
- Compared to reference gasoline and Alaska North Slope crude oil.
- ASTM D4294 for sulfur in petroleum products. Positive and negative controls included.
- ASTM D5453, more sensitive.

Tier 2:

- Volatile PIANO Analysis - US EPA SW-846 8260D
 - Quantitative analysis of 11 paraffinic, 37 isoparaffinic, 50 aromatic, 14 naphthenic, 22 olefinic compounds.
 - Positive and negative controls.
- Alkyl Lead Compounds - US EPA SW-846 Methods 3580A and 8270E

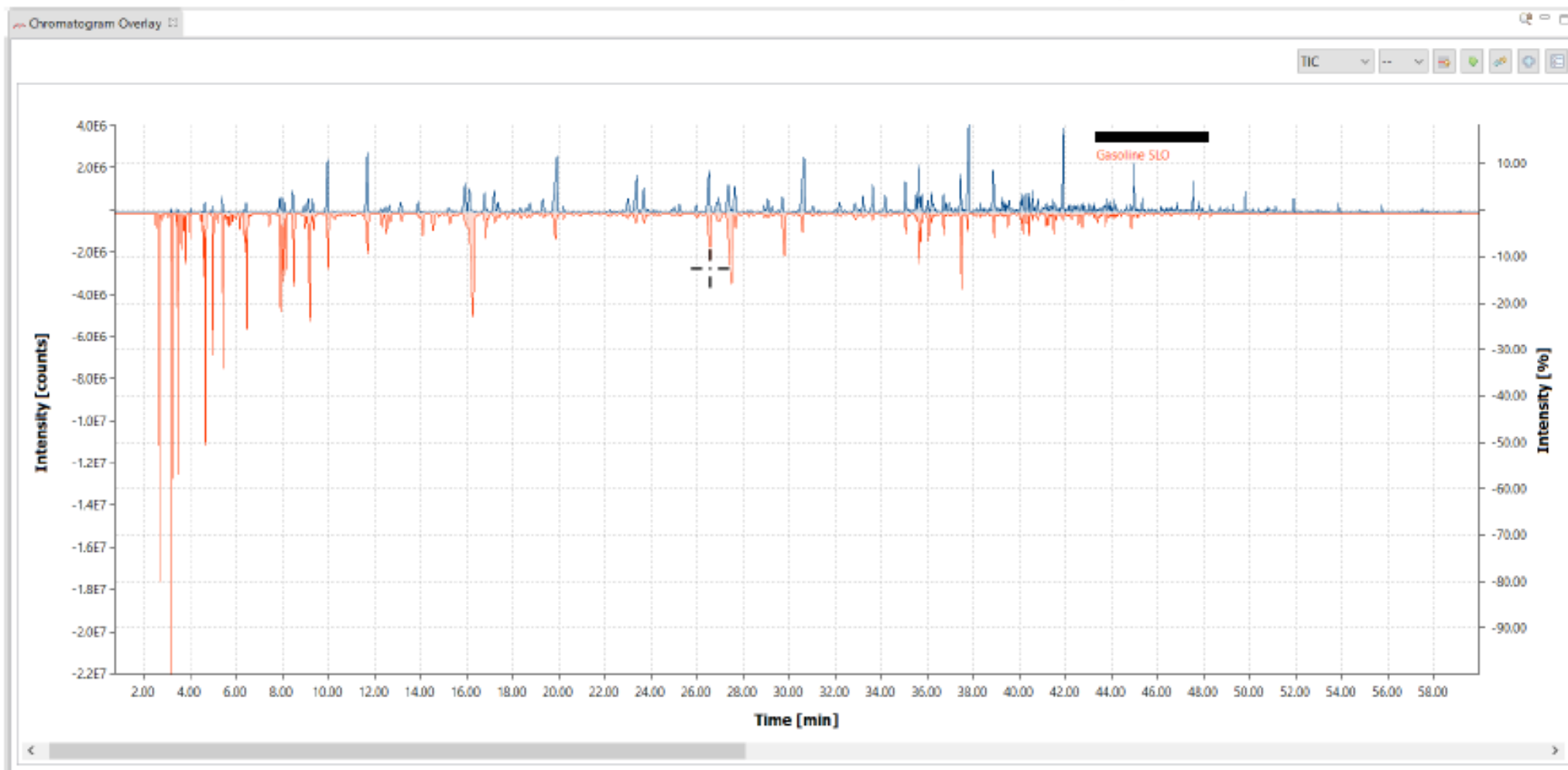
Method and Forensic QC Checks

- Blanks, Calibration, Surrogates, Internal Standards as applicable.
- Alkane marker, retention time stability, peak shape, symmetry, resolution.
- Mirror overlays to identify carbon ranges in whole oil analysis.
- PIANO classified as in Example 1 with radial charts.
- Diagnostic ratios for refining, isomerization, aging (n-C₁₇:Pristane), weathering differences for gasoline.

Reference Gasoline – Sample MW-XX overlay

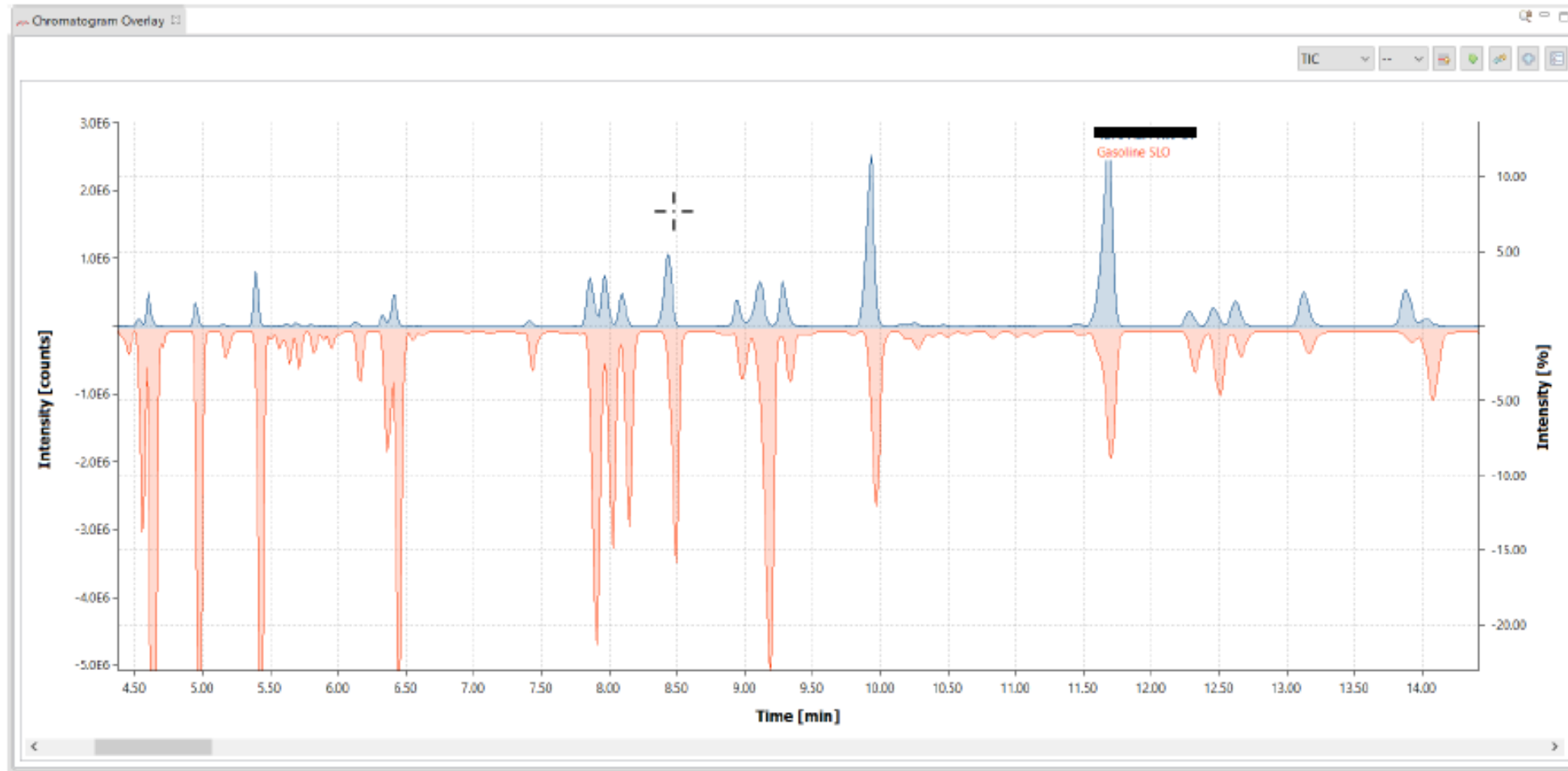


Site Gasoline – Sample RW01 overlay



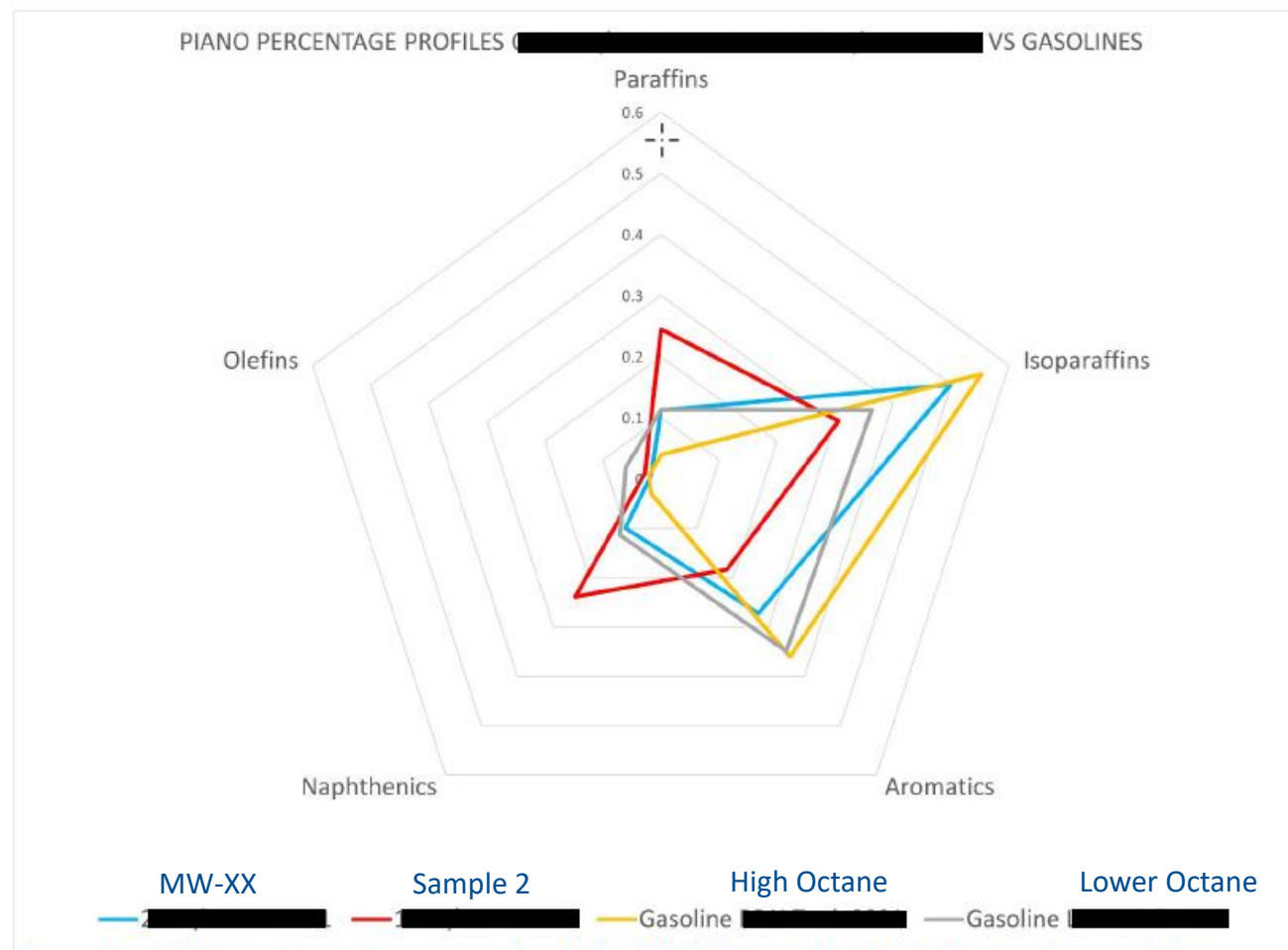
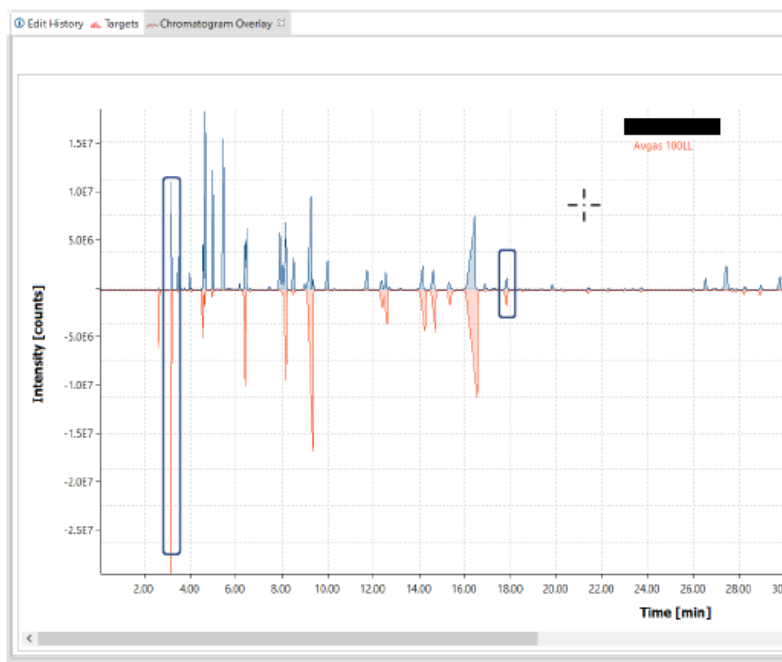
Loss of light range,
toluene not significant
vs prior sample

Site Gasoline – Sample RW-XX overlay expanded view



Gasoline
match but
with loss of
lighter MW
components

Site Gasoline – Sample MW-XX overlay



Tetra-ethyl Lead and Sulfur

Sample	TEL (mg/kg)	Sulfur (mg/kg)	Age Inference
MW01-A1	103	105	TEL indicative of leaded gasoline after 1985. Sulfur consistent with 2005 cap of 300 ppm
RW01	20.2	1950	TEL below current caps. S in range of historical untreated gasolines
MW01-BM	453	189	TEL within 1982-1985, though could be from site. S above 2005 cap, possible loss via weathering
Reference Gasoline	684	274	

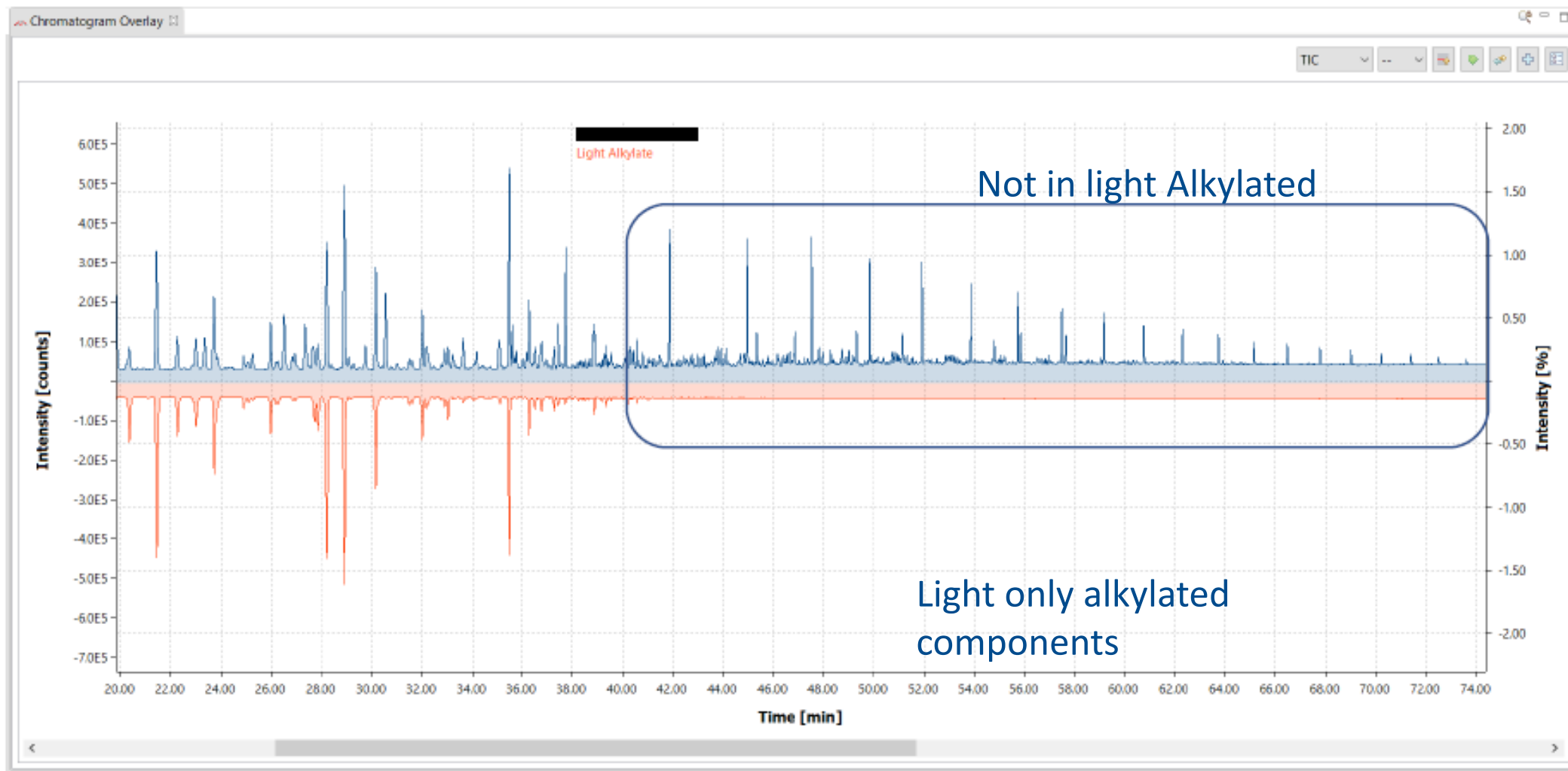
Calculated TEL (mg/kg) in Gasoline time periods

Average prior to 1978: 1996

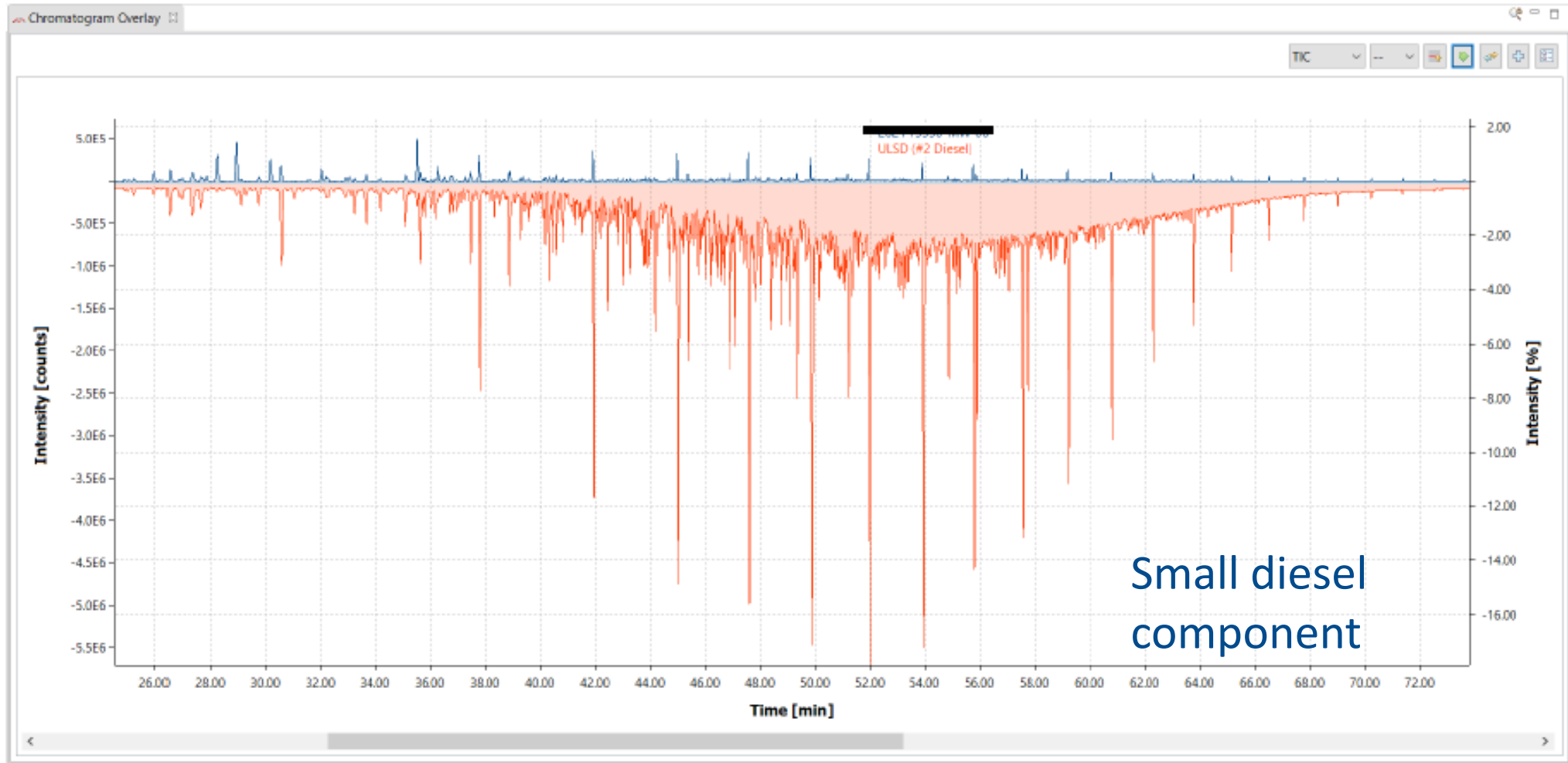
Federal Cap 1982-1985: 627

Federal Cap beginning 1985: 285

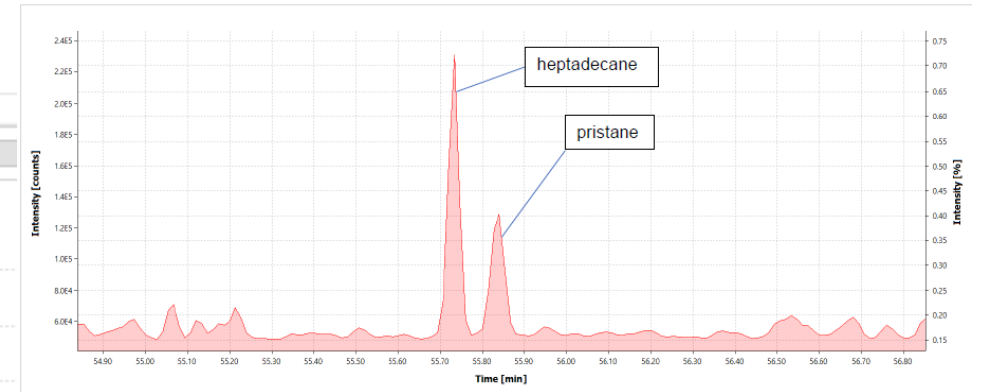
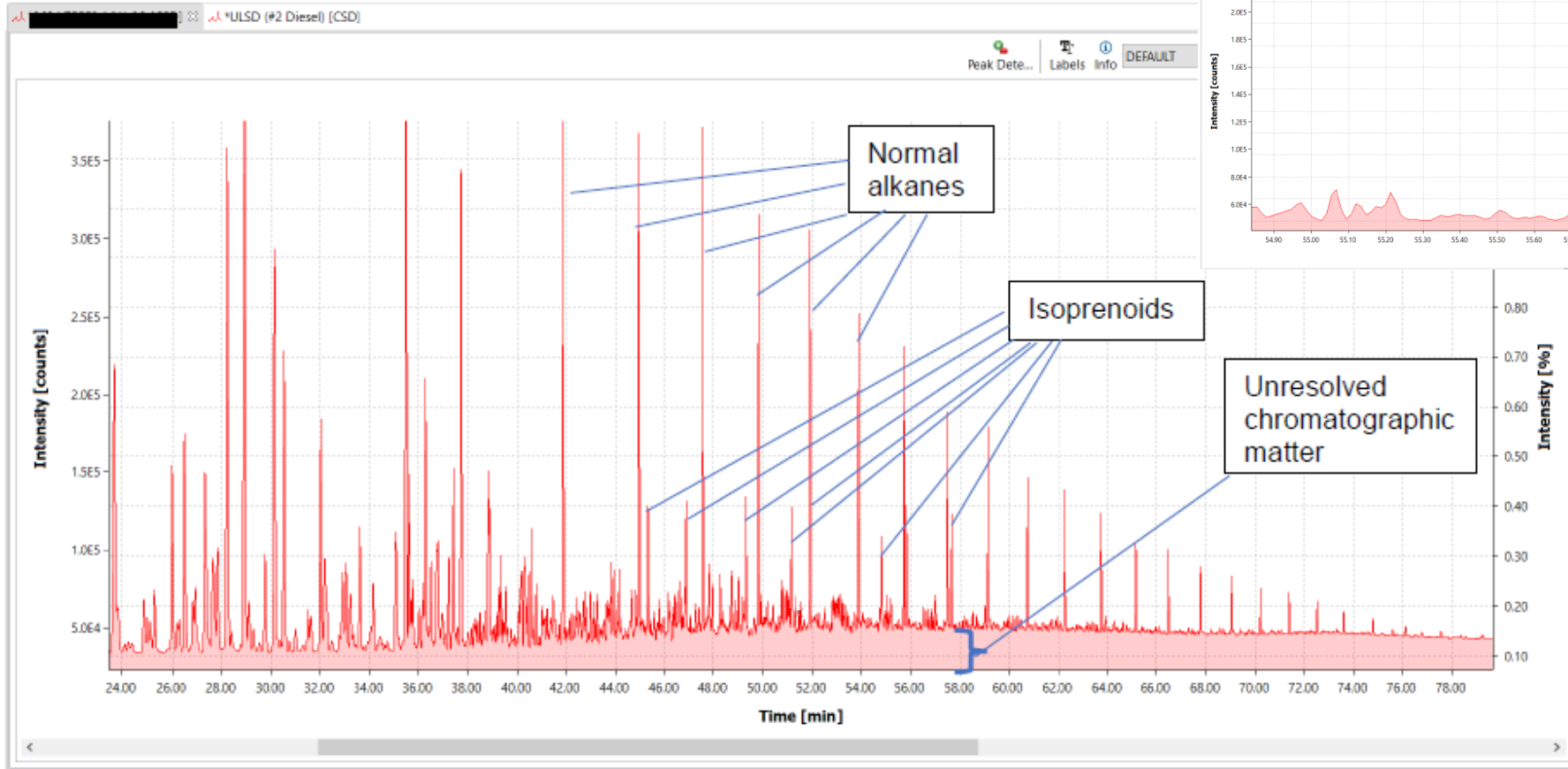
Example 3 – Composite



Example 3 – Composite



Example 3 – Diesel Component



Mix of light alkylate with C₆ naphthenes, paraffins, and isoparaffins. Undegraded diesel fuel secondary component

Thank You QUESTIONS?



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