Field Analytical Method Development for C_6-C_9 Range Hydrocarbon Measurement

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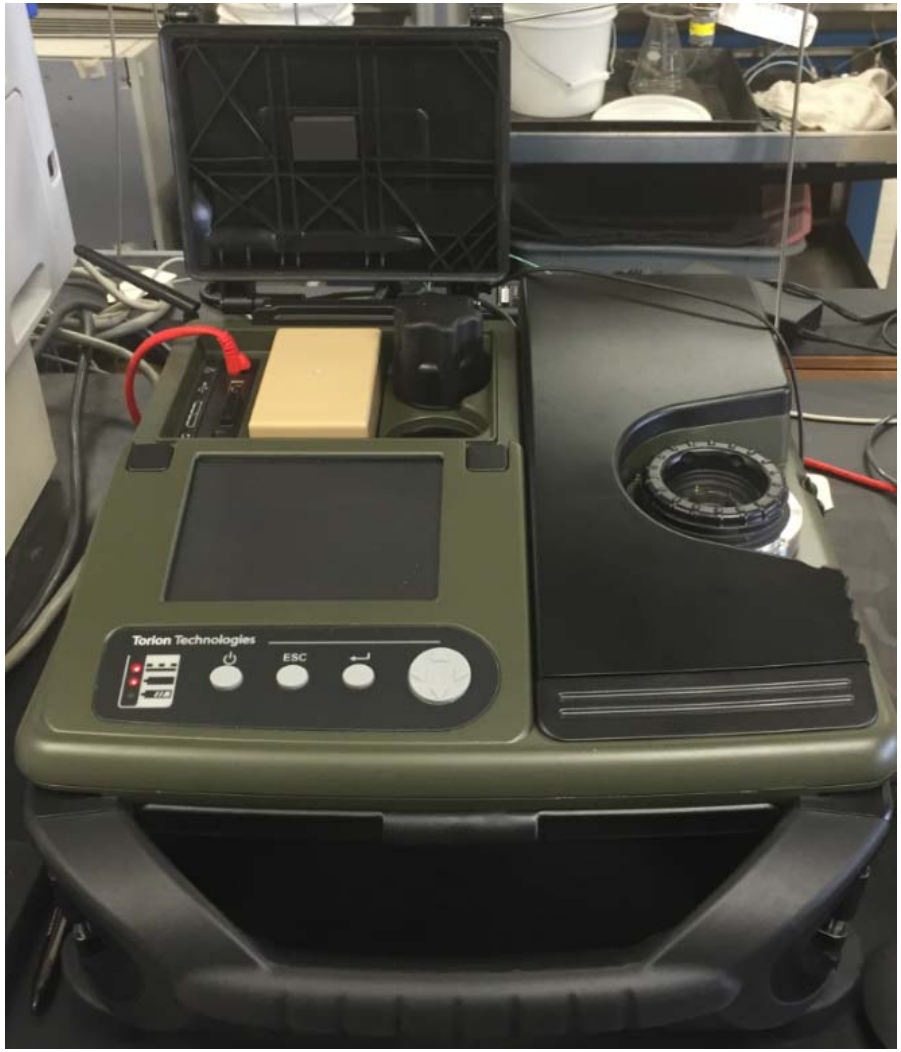
Project Background and Objective

- Data gap was identified during 2016 delineation work plan approval process.
- Develop simple field screening method for C_6–C_9 petroleum hydrocarbon (PH) in soil using portable GC-MS and headspace sampling.
- Demonstrate detection limit of C_6–C_9 PH of 50 ppm or below.
- Meet regulatory requirement for soil segregation and remediation.
- Secondary objective is to measure the benzene concentration in soil samples.

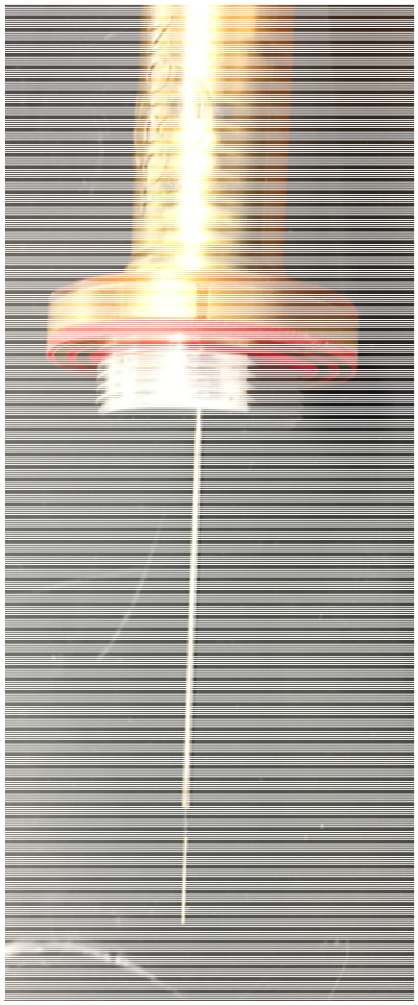
Torion T-9 Portable GC-MS

- Torion T-9 Portable GC-MS.
  - Portable instrument for field use.
  - Rapid sample analysis.
- Fast chromatography using LTM-GC.
  - Low thermal mass (LTM) gas chromatography (GC).
  - Short metal capillary column.
  - Cycle time of less than 5 minutes.
- Miniature and high sensitivity mass spectrometer for identification of compounds.
  - Toroidal ion trap mass spectrometry.
  - Ions trapped and ejected by radio frequency, yielding m/z values.



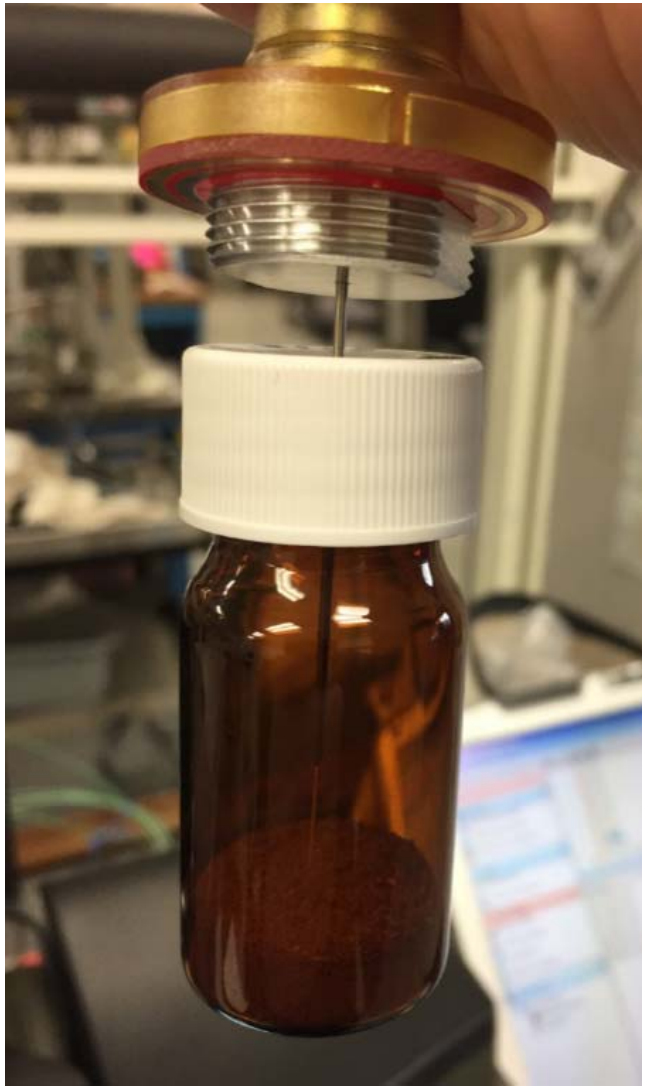
Sample Injection

- Solid Phase Microextraction (SPME) syringe.
  - 19 gauge needle.
  - 1 cm fiber coated with DVB/PDMS polymer.
  - Vapor phase molecules adsorb to the fiber.
  - Molecules compete for fiber locations based on DVB & PDMS affinity.



Field Sampling and Testing Protocol

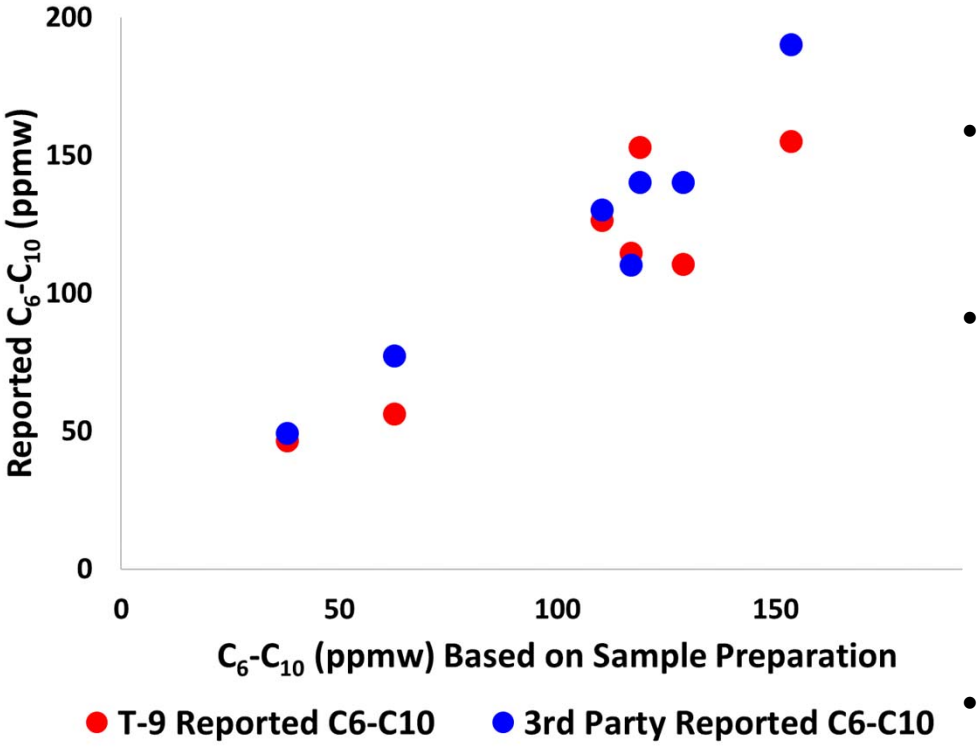
- 5 grams of TPH contaminated soil in a 20 mL VOA vial with a septum cap.
- SPME syringe to collect headspace.
- Agitate soil in VOA vial to liberate C_6-C_9 range molecules.
- 1 minute sampling of headspace.
  ~ 1 cm above soil.
- Inject SPME syringe into T-9 GC-MS.
- External calibration with crude oil with known C_6-C_9 and benzene content.
  ~0.02 g crude oil in 5 g blank soil.



T-9 External Calibration by ASTM D7900

- The data quality objective is to measure C_6-C_9 in soil originating from crude oil.
- Unlike GC-FID, GC-MS has significantly different response factors for compounds.
  - Crude oil contains over 100 hydrocarbon compounds in the C_6-C_9 range.
- Certified GRO standards are typically composed of gasoline type material.
  - Gasoline has a different hydrocarbon composition compared to crude oil.
- A crude oil has been used as the calibration standard with no solvent present.
  - Typical solvents interfere with the T-9 analysis of the C_6-C_9 range.
- ASTM D7900 by GC-FID is the preferred method for measuring C_2 to C_9 compounds in stabilized crude oil.
  - Internal lab certified the crude oil standard to be C_6-C_9 = 15.97 weight % and Benzene = 0.36 weight %.

Method Verification

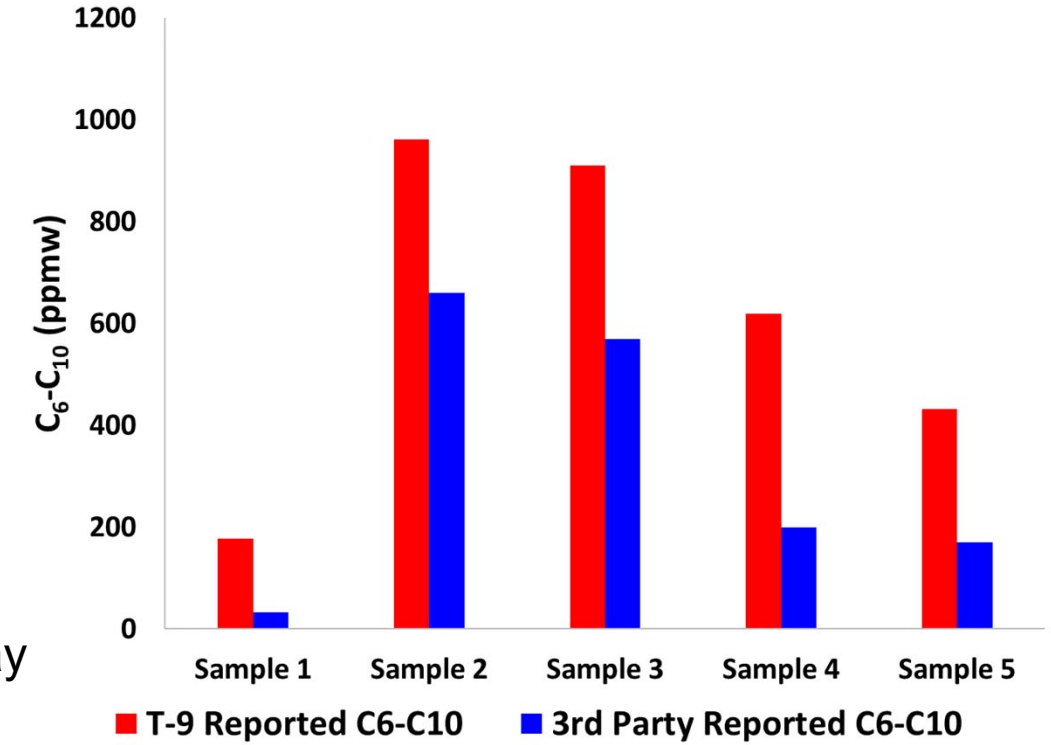


- Crude oil with ASTM D7900 certified C_6-C_9 content and certified blank soil.
- Prepared soil samples with varying amounts of crude oil.
- Samples split for comparison with a 3rd party lab.
  - Chevron lab T-9 GC-MS
  - 3rd party lab EPA Method 8015B (GC-FID).
- Duplicate injections were performed on the T-9.

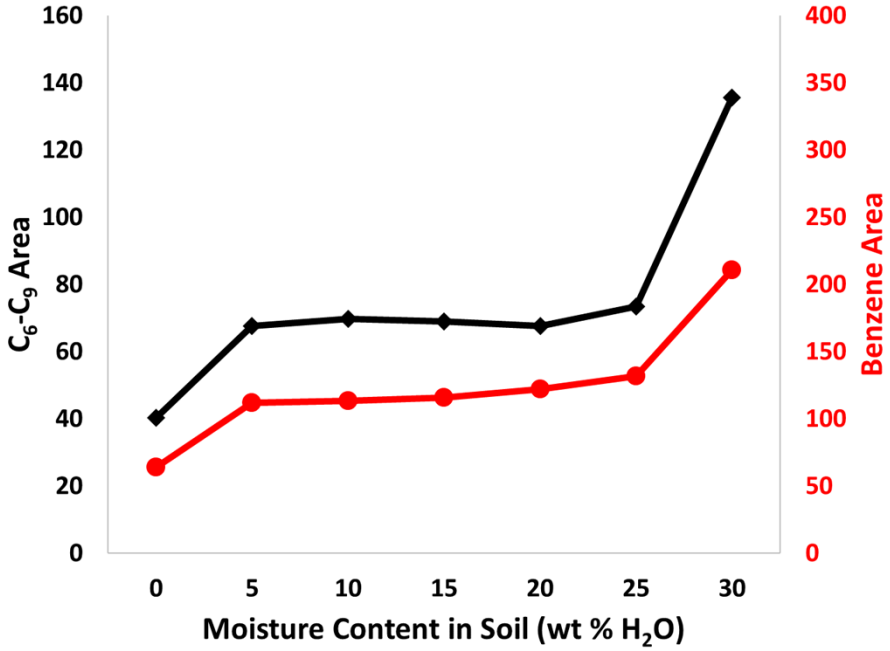
Method Bias Evaluation

Measure the method bias with field sample tested by a conventional lab method.

- Soil samples collected at a former oil field and shipped to Chevron lab.
- Samples split in the lab for comparison with a 3rd party lab.
  - Chevron lab T-9 GC-MS
  - 3rd party lab EPA Method 8015B (GC-FID).
- T-9 results are higher for the field samples compared to the 3rd party results.
  - Heterogeneity of the samples may have caused the discrepancy.
  - Different analytical methods.
  - Different calibration standard.



Impact of Soil Moisture Content

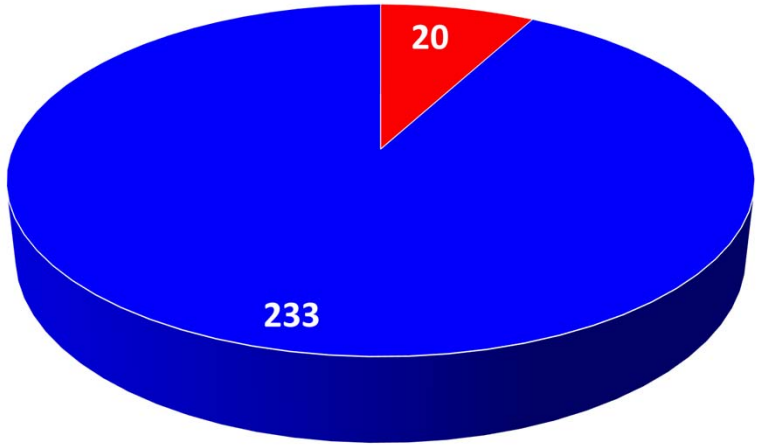


- Crude oil with ASTM D7900 certified C_6-C_9 and Benzene content.
- Certified blank soil.
- Vials spiked with varying amounts of deionized water by weight.
- Shake the vials vigorously to mix the soil, crude oil, and water.
- All of the vials containing water had some soil adhering to the vial wall.
- The 30% water vial had a significant amount of soil adhering to the vial wall and did not mix well.

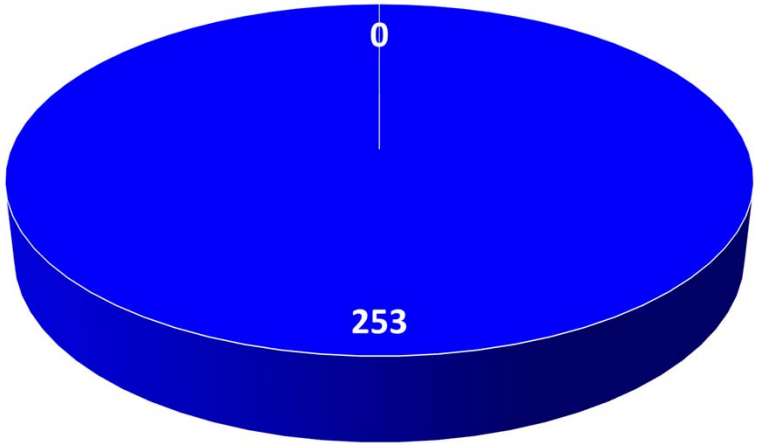
Portable GC-MS Field Pilot Results

- 253 freshly collected soil samples over the course of 10 days from a crude oil production field.
- 166 soils contained variable concentration levels of TPH, as reported by EPA Method 8015C.

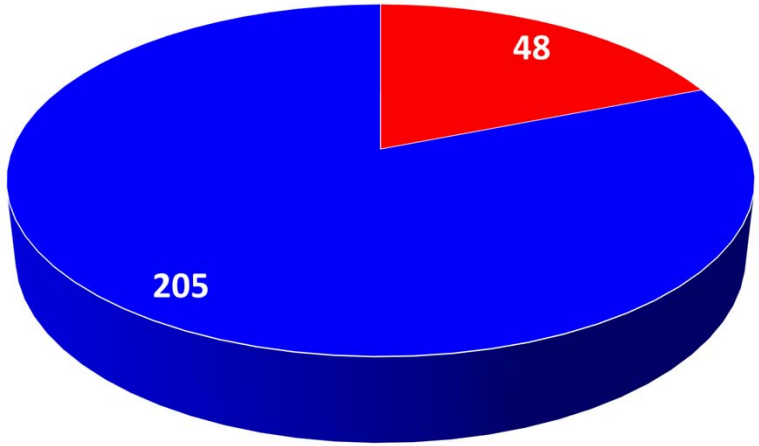
Red = C_6-C_9 >= 100 ppmw



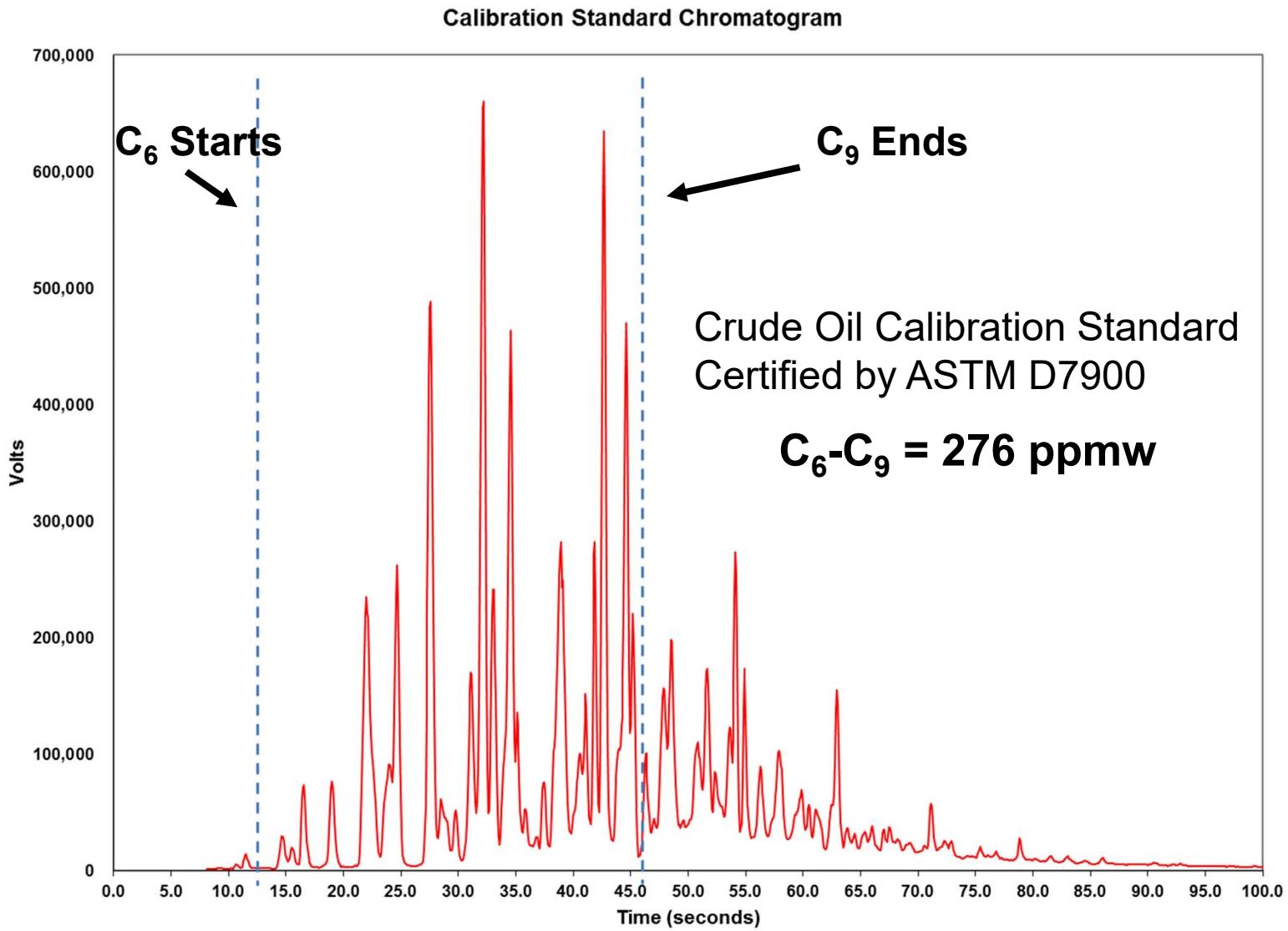
Blue = Benzene = 0 ppmw



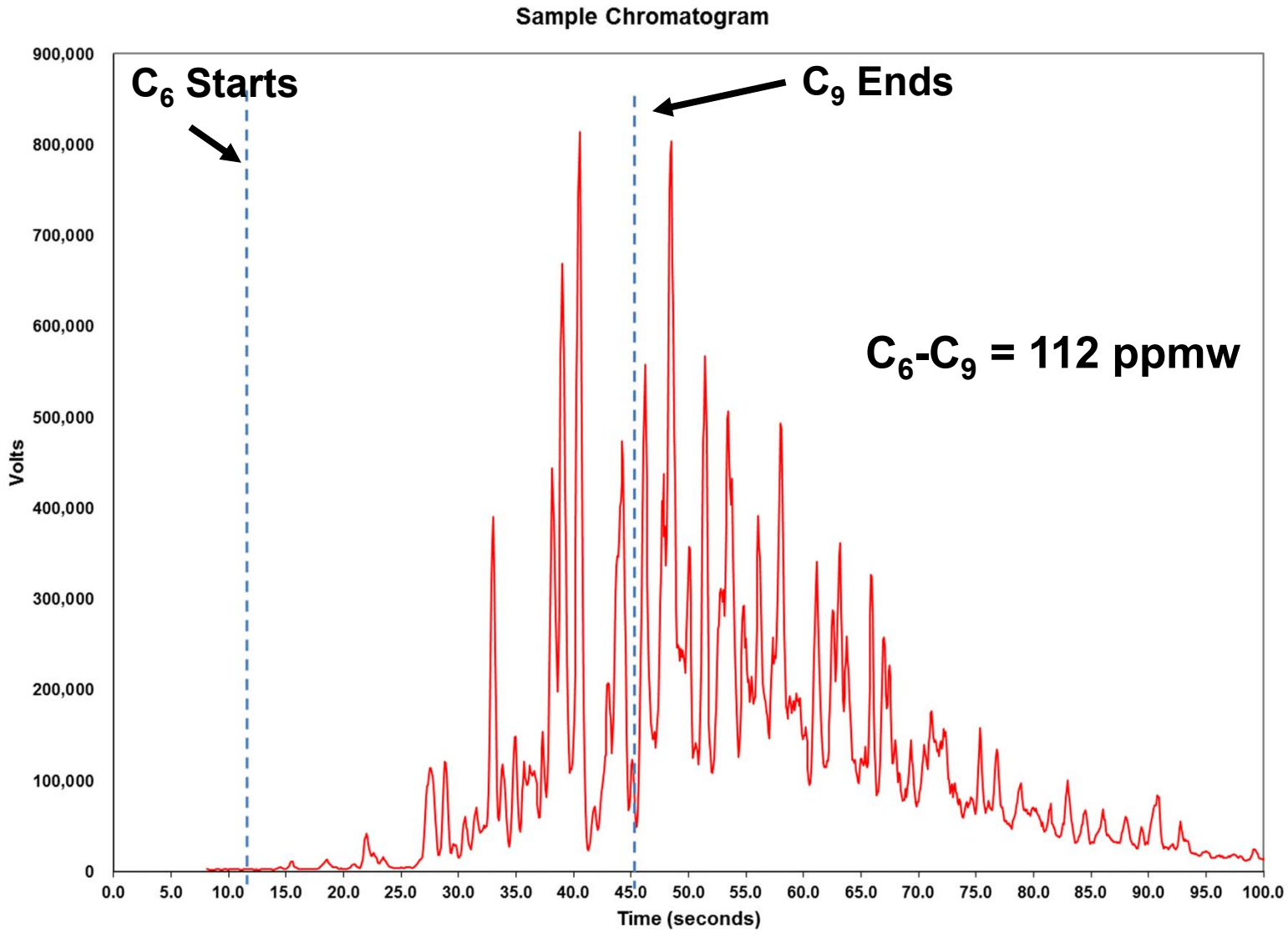
Red = C_6-C_9 >= 25 ppmw



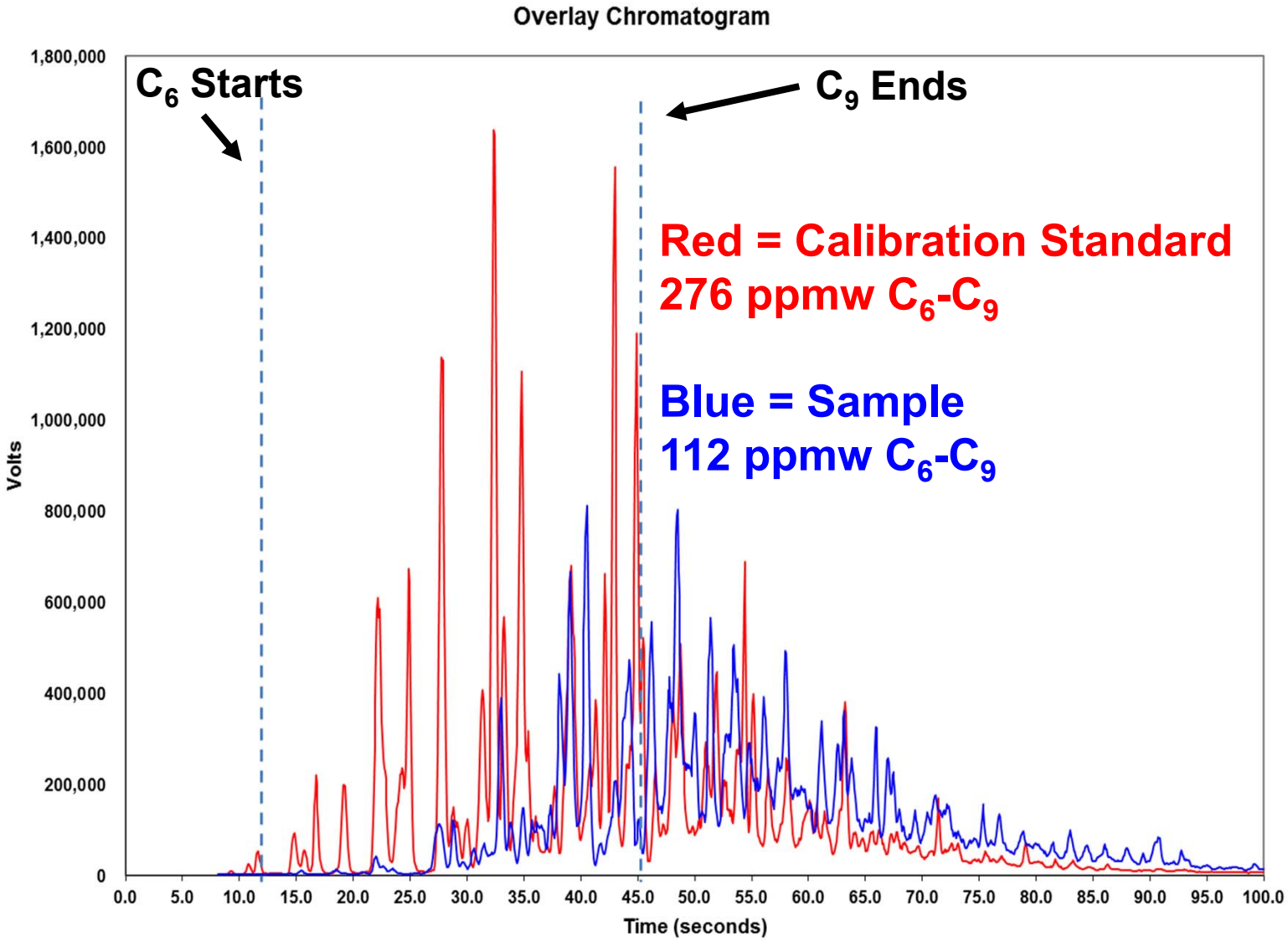
TIC – Calibration Standard



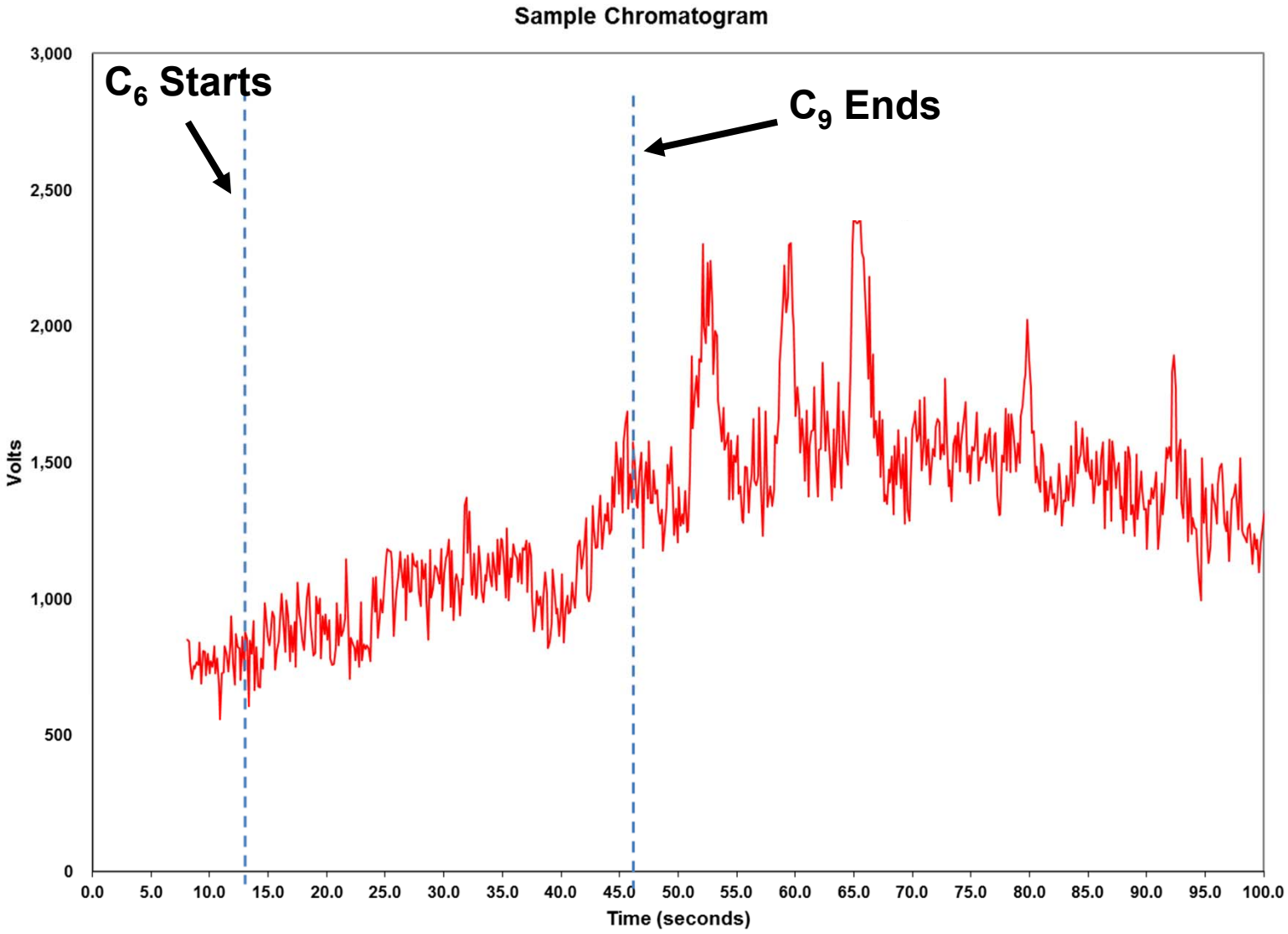
TIC – Sample Containing C_6-C_9 >= 100 ppmw



TIC – Sample Containing C_6-C_9 >= 100 ppmw

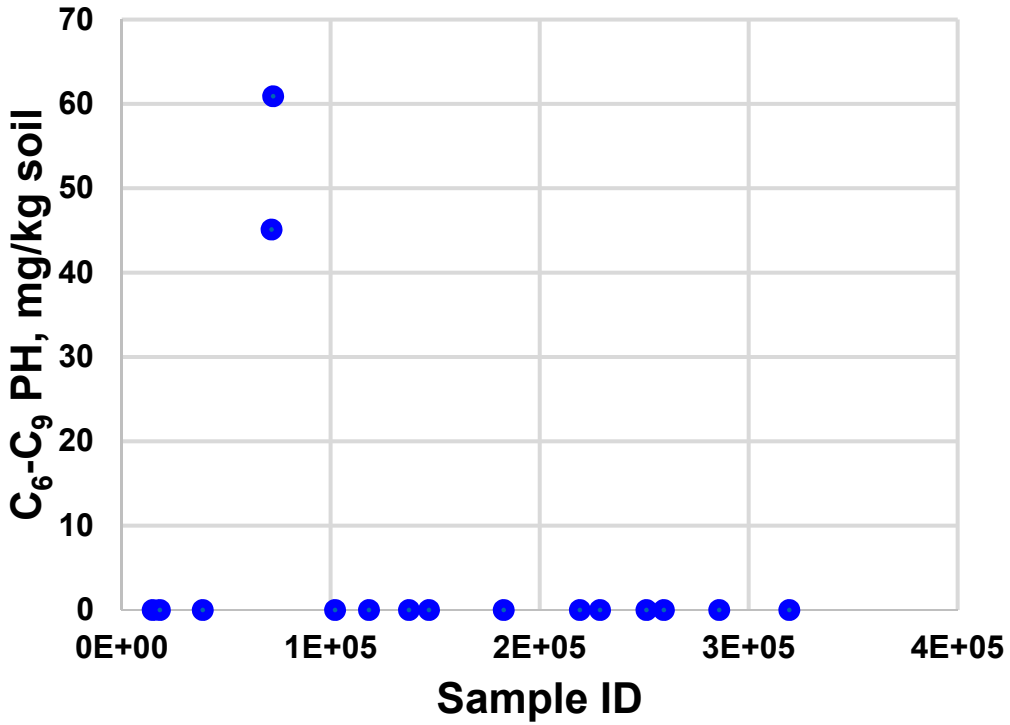


TIC – No C_6-C_9 Present



Field Pilot Comparison with 8260B

- 3rd party lab performed EPA Method 8260B with a Purge and Trap (PT) device and soil samples were prepared using modified EPA Method 5035.
- Possible reasons for data variation.
  - VOC loss due to sample handling in a hot humid field.
  - Sample introduction techniques- Headspace Injection vs. PT
  - Calibration



ND = Below detection limit 40 ppm

Soil Appearance

C_6-C_9 = 80 ppmw

C_6-C_9 not detected

Samples can look similar but contain significantly different C_6-C_9 ranged material.

Summary

- This portable GC-MS instrument will enable rapid C_6-C_9 screening data collection in the field.

- Significant time reductions for labs relying on third party data.
  - Real-time process monitoring.
  - Rapid, field-based testing.
  - Easy to operate.

- Improved safety by elimination of solvents.
  - Prevents worker exposure.
  - Eliminates generation of waste.

- Potential Cost Savings.