Risk-Based Characterization and Assessment of Extractable Petroleum Hydrocarbon Contamination Using Comprehensive Two-Dimensional Gas Chromatography with Dean's-Switch Modulation

1

Approximately ten years have passed since the first generation of risk-based petroleum methods was developed and put into production in the environmental laboratory. Advances in gas chromatographic flow control technologies can now be used to replace the tedious sample preparation techniques previously required to obtain the separate sample extracts ("fractions") used for site characterization/assessment.

In this new approach, a single total petroleum hydrocarbon (TPH) methylene chloride extract is analyzed using a two-dimensional gas chromatograph (2-d GC; GC x GC) designed to separate the aliphatic and aromatic species using flame ionization detection (FID). This updated method meets the original intent of the Massachusetts state and TPH Working Group methods.

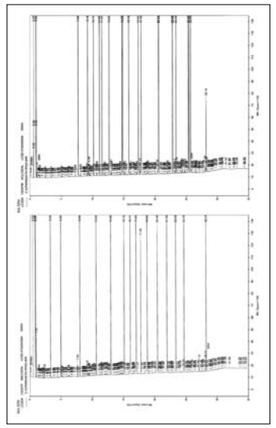
2

Challenges of "Classic" Fractionation Method

- Invasive prep procedure
- High consumables cost
- Highly technique-dependent
- Variability in reagents/media, etc.
- Long analysis time
- Lenient acceptance criteria

3

Scenario A:
Successful Fractionation



Scenario B:
Poor Fractionation; unacceptable breakthrough of naphthalene and 2-methylnaphthalene into aliphatic fraction (13% and 9%, respectively). Retention of aliphatics on silica gel column. Aliphatics end up in Aromatic fraction.

4

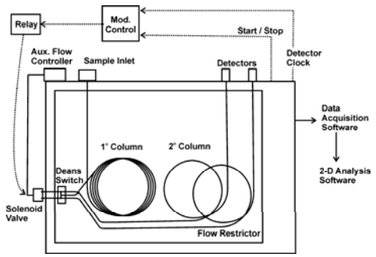
Challenges Addressed

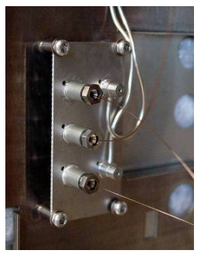
- No loss in sensitivity, accuracy or precision.
- Easy to implement in lab production environment with minimal capital investment.
- Exploit differences in two dimensions (boiling point and polarity) to separate target species chromatographically using opposing GC column phases instead of relying on tedious prep.
- Reagent volume and cost will drop.
- Time saver / money saver.

5

A Microfluidic Deans Switch As A GC x GC Modulator

Agilent Deans switch etched onto a metal plate.
Rugged device with a very wide temperature range and inert surfaces.
Direct diversion modulation with no temperature restrictions.





6

Analysis Conditions/Parameters

Agilent 6890 fitted with Agilent Dean's switch flow modulator set to 1 sec modulation period. 0.07 duty cycle.

Cool on column injection of 1ul. Inlet temp tracked ~ 3C above oven temp.
1 m x 0.32 mm fused silica retention gap ("guard column")
Primary column: DB-17ht (45M x 0.25mm x 0.15um)
Secondary column: DB-1ht (2.5M x 0.25mm x 0.1um)

FIDs @ 340C

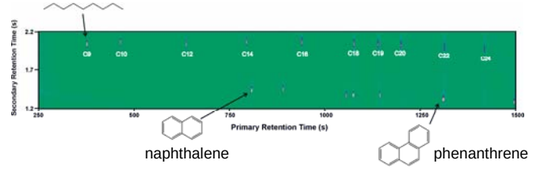
Carrier gas: Hydrogen
Primary flow: 1 ml/min
Secondary flow: 10 ml/min split between the 2o column and flow restrictor.
Oven Program: 40C for 3.25 min; 13C/min to 70C; 10.5 C/min to 120C; 9.5C/min to 340C; hold @ 340C 5 min.

Run time: 35 minutes

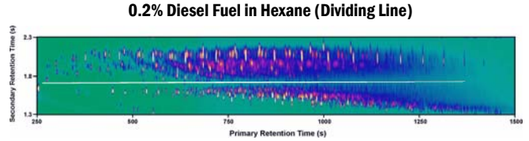
FIDs were set at 340 oC

7

Examples of Two-Dimensional Chromatograms



0.2% Diesel Fuel in Hexane (Dividing Line)



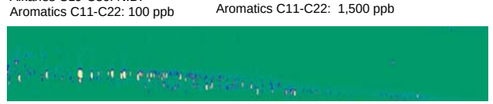
8

LCSD for water sample.
Components are 40 ppm in CH2Cl2.
Calibration results correctly predict concentrations to within 5%
This picture shows the spatial ranges of the n-alkanes and PAHs.
File Name: 1218LCD2

Sample #: 4912819
GC File Name: 121819

Reported Concentrations
Alkanes C9-C18: 350 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 100 ppb

GCxGC Measured Concentrations
Alkanes C9-C18: 25 ppb
Alkanes C19-C36: N.D.
Aromatics C11-C22: 1,500 ppb



9

Analysis of Soil Samples

- Switched to ZB-50 Primary column and DB-1 secondary column.
- Same tailing issues as DB-17ht x DB-1ht combination.
- Recalibrated system.
- Checked calibration with LCS and LCSD mixtures and got excellent agreement. (95% certainty)
- Analyzed soil samples.

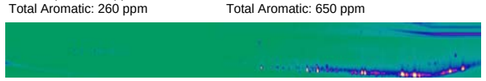
10

Sample #: Level 4 Std (20 ppm of each compound)
GC File Name: 0214CS4

Sample #: 4957951 (5X dilution)
GC File Name: 021551_5

Reported Concentrations
Total Aliphatic: 70 ppm
Total Aromatic: 260 ppm

GCxGC Measured Concentrations
Total Aliphatic: N.D.
Total Aromatic: 650 ppm



11

Challenges Met

- More accurate/precise data.
- Perform "routine" TPH extraction. No need for solvent exchange, multiple concentrations or fractionation steps.
- Minimal hardware/software upgrades.
- Simplified prep procedure results in only one sample extract for analysis, cutting run time in half.
- Easy to implement without sacrificing extra lab space.

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