Use of Fast Gas Chromatographic and Chemometric Technologies for Hydrocarbon Characterizations from Exploration Activities to the Refinery Floor and Beyond

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Petroleum Value Chain
From Discovery to Customer Use

EXPLORATION
- Basin & Prospect Value Risks
- Crude Assay
- Rock & Fluid Characterization
- Reservoir models

PRODUCTION
- Reservoir Performance
- Oil Field Chemicals

TRANSPORTATION
- Flow Assurance
- Corrosion/Scale
- Processing/Separation
- Environmental
- Blending/Dilution
- Upgrading/Refining Processes
- Refinery Operations
- Crude Assay

REFINING AND RETAIL
- Product Quality
- Environmental

$ $ $
From discovery to abandonment, from ingredient to finished product, gas chromatography plays a prominent role in hydrocarbon evaluation.
Attainable Yield Roadmap
GC Applicable to Most Refinery Streams

Stream Color Key
- LPG
- Gasoline
- Distillate
- VGO
- Resid

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Unfortunate Trend
(Reduced Skill Sets and Manpower)

UBS newsletter, *Investment Intelligence*: As baby boom US workers retire, we create a shortage that follow-on generations have neither the numbers nor the skills to fill.

And from the Gulf Coast Conference (ca. 2005) -

Randy Shearer, Rentek: We are graduating fewer scientists and engineers in the US. We need to apply the continuing improvements in computer technology.

- Chromatography is a key area
- In GC, that means faster analysis

Bill Winniford, DOW: We have to make do with a lot fewer people and they will have more to do. We are entering a time we have never seen before.

- Chief frustration is in data processing
- Not good at capturing knowledge from the experienced workforce
Comparison of Spectroscopy and Chromatography
(conventional wisdom)

Spectroscopy is faster (~1 minute per run)
Plumbing is slightly simpler
Maintenance is slightly easier

Speed favors spectroscopy
Information content favors chromatography
Overall cost of ownership is about the same

Chromatography is slower (~30 minutes per run)
System response is largely linear over a wide concentration range
Concentration of individual components is measured more directly
Speed of Analysis

If we are really going to use GC for control, speed means under 10 minutes for most applications.

Poll of Process Users
Routine use of fast GC means:

- Lots of data: 20 results per hour (~500 per day)
- Lots of interpretation (are the results correct?)
- Lots of opportunity for errors
- Drives the need for automation
  - analysis
  - data collection
  - preprocessing
  - interpretation
  - system suitability assessment
  - results
  - result validity
  - fault identification
  - pass/fail

Therefore ... Chemometrics!
Sweet Spot in GC Technology
(Moving to smaller, faster yet capable systems)

- Siemens Maxum II
- Agilent 7890
- Falcon Calidus
- Thermo C2V-200

Application Capability vs. Speed

High

Low

Fast

Slow
Downstream Fingerprint/Yield Applications

Example: FCC Feed

Example: Sulfur in Crude Fraction (Diesel Range)
ASTM D 2887 Reproducibility

(6 min run for Gas Oil)

### Boiling Point Table (%Off)

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### Table Notes

- **IBP (Initial Boiling Point)**
- **FBP (Final Boiling Point)**
- **%Off** represents the percent deviation from the specified boiling point.
- **Avg** is the average value of the measured boiling points.
- **%SDV** is the standard deviation of the measured boiling points.

### Graph Notes

- The graph shows a time series plot of Signal (mV) over Time (Min) for the ASTM D 2887 test.
- The peak points indicate the boiling points at various %Off values.

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Implications of fast GC use

• GC provides for more information content than spectroscopy, but deployment of the more complex chromatographic systems on-line lags due to our need to do some handholding of each run - human review.

• The problem (unless there is a plug) is not in the intensity axis, the problem is that the peaks can move in the time domain.

• We need another tool in our kit to reduce the time domain variability, and thus reduce the level of skill and manpower needed to ensure we meet our data quality objectives.
Automated alignment works - 1

Alkylates:
5 year period, 6 GCs
Automated alignment works - 2

Alkylates:
5 year period, 6 GCs
Repeatability for a Process Based MicroGC
(Native Repeatability - 2 weeks 6 minute cycle time)

Start to 650°F
Sample of a Conventional Crude Oil

Above: 3.5 min run
Right: expansion from 0.4 to 0.6 min.
Repeatability for a Process Based MicroGC
(Following Alignment and Normalization)

Substantial Reduction in Sample to Sample Variability

Above: 3.5 min run

Right: expansion from 0.4 to 0.6 min.
Direct Comparison of Native versus Align/Normalized Chromatograms

Region from 1 to 2 min displayed

Variation reduced by a factor > 20 with alignment

SimDis Statistics

- Average: 1.7°F
- Minimum: 0.3°F
- Maximum: 4.9°F
Comparison of Native to Aligned Chromatograms (Extended Test)
Increasing Automation

• With alignment automated into the system, the next step is to build confidence that any degradation in chromatographic separation won’t cause problems or flag that there is a problem that needs human intervention.

• For many applications there is retention time to spare and research grade GCs are overkill.

• The goal is matching the resolution and speed requirements for any measurement with minimal overhead.
Information content maintained at faster speeds: Data from μGC, lab GC, and process GC

The yield curves match thanks to LineUp Alignment

4 minute cycle on Calidus versus 1.5 hour cycle on an Agilent 6890
Polywax Standard

Allows transformation of retention time to a different basis (e.g. carbon number or boiling point)
Representative Chromatogram for a Drill-stem test
(Heavy Oil)
Overlay of a series of heavy oils
(Various fields)
PCA Scores and HCA Dendrogram of Oil Types

Automated assessment of field similarity and/or continuity.
Establishing Oil Classes
Chemometrics enables plug-and-play GC

We can correct retention times to match an application-specific relevant sample

This eliminates the transfer of calibration problem

Common regression and classification algorithms can be applied automatically to infer physical properties or characteristics

This allows us to bring more complex analyses into on-line use

With the current line of instrumentation, GC fast enough to allow true control even in complex analyses
Summary

• We are never going to displace spectroscopy’s *analysis at the speed of light*, nor do we want to.

• But, as the GC cycle time changes from hours to minutes, the information content inherent in the chromatogram makes it extremely valuable for complex mixtures – *a little bit of separation goes a long way*.

• For petroleum composition understanding, *slice and dice*, is the only way.
Questions?