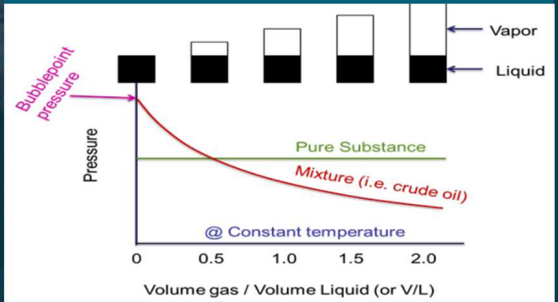
SAND2019-13317C

Crude Oil Compositional Analysis Methods and Their Impact on Thermophysical Properties



PRESENTED BY

Joseph W. Hogge, Ph.D., Sandia National Laboratories

David L. Lord, Sandia National Laboratories

Raymond G. Allen, Allen Energy Services, Inc.

David K. Rudeen, GRAM, Inc.

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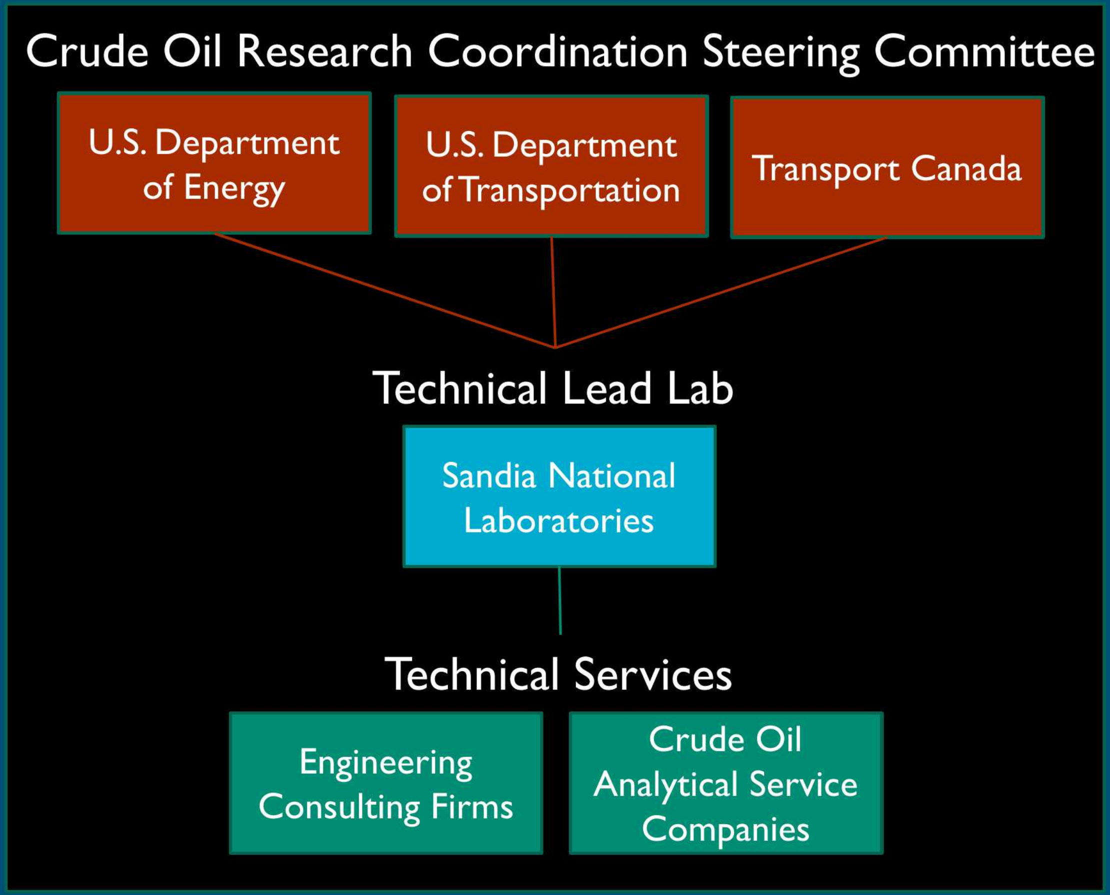
Project Governance

Crude Oil Characterization Research Study



Problem Statement

What is the **best analysis method** to acquire the **compositional data** necessary to successfully simulate **shale oil vapor pressure**?

Methods

The focus for this work was on getting accurate data for **VPCRx(100°F), V/L=0-4** in conditioned shale oil. This property can be measured or calculated (from compositional data using an EOS).

- Measure VPCRx and whole oil composition of shale oil

- **Baseline Method:** tight-line sampling into a flash separator with coupled analysis; deployed at the U.S. Strategic Petroleum Reserve
- **Test Methods:** commercially available analysis methods using 1-L "closed" spot samples

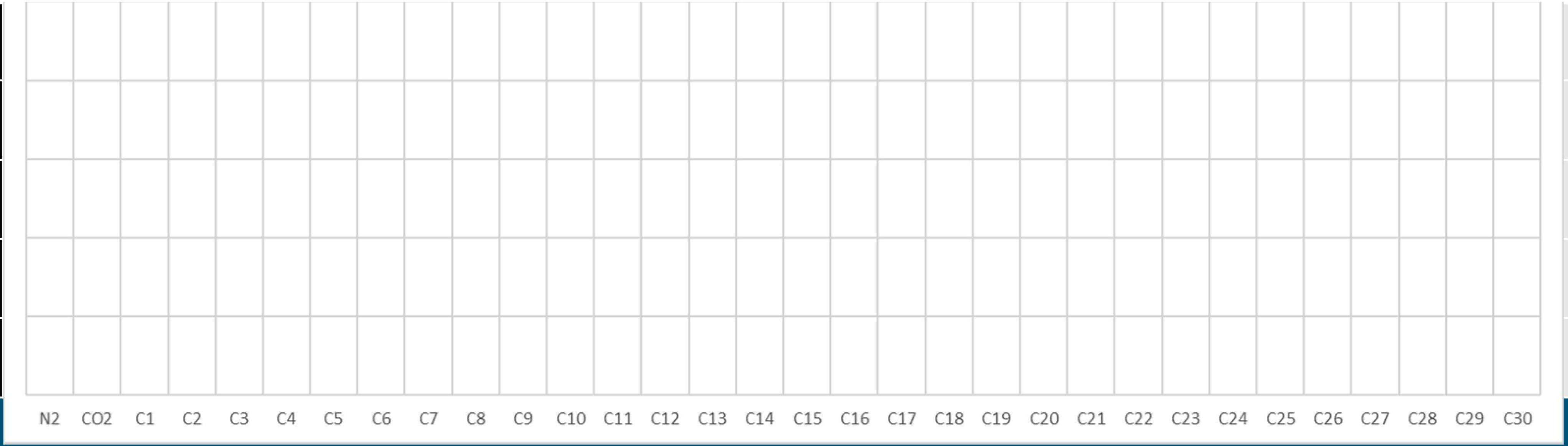
Glossary	
VPCRx(100°F)	Vapor pressure of crude oil at 100°F and V/L = x
V/L	Vapor-to-liquid volume ratio
EOS	Equation of state model
Whole oil composition	A set of compositional data where each constituent is quantified on the basis of the whole sample
"Closed" spot sample	Pressurized spot sample that was collected so that the sample did not contact atmospheric conditions

picture used with permission from Intertek

Compositional Methods

Multiple analysis methods assembled into whole oil compositions using merge techniques

Name	Carbon Number Applicability Range	Notes
TM1		
TM2		
TM3		
TM4		
TM5		



- the carbon number associated with the residual for a given single method

- high measurement uncertainty regions.

- physical property used in merge.

- residual fraction assumed to be accurate for a merge of two methods.

Compositional Methods

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Name	Carbon Number Applicability Range	Notes
TM1		Baseline; tight-line flash recombination
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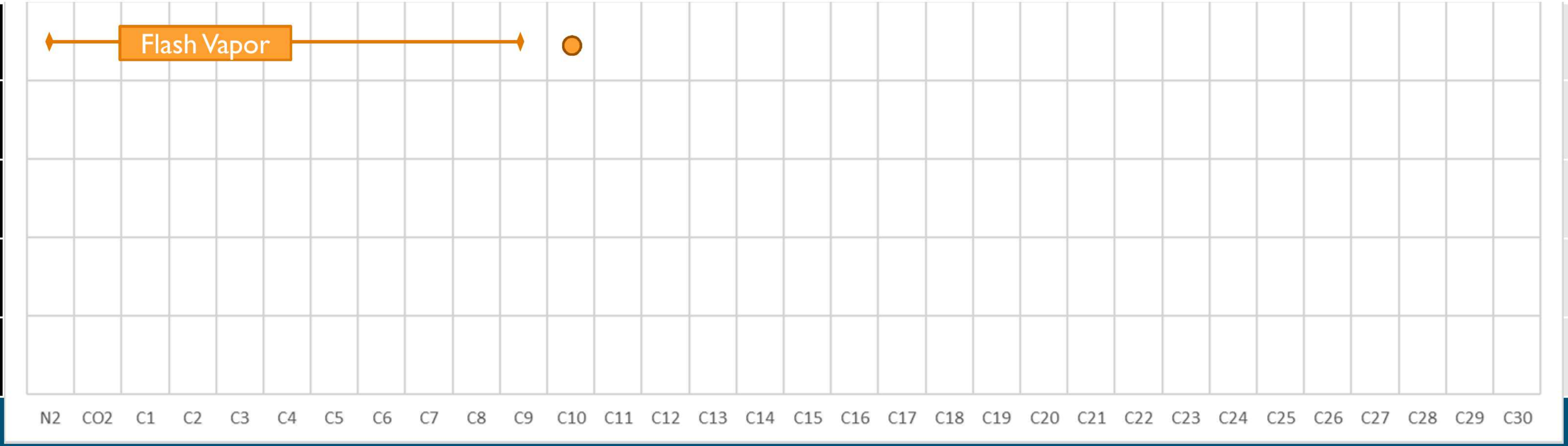

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Name	Carbon Number Applicability Range	Notes
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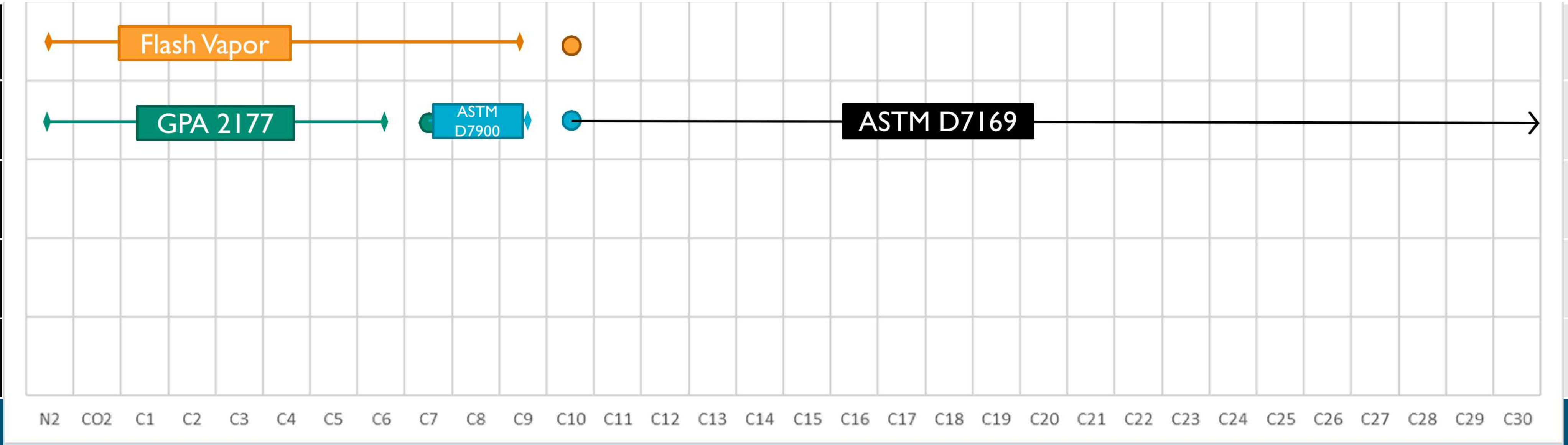
TM2		All GC methods
TM3		
TM4		
TM5		



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Compositional Methods

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Name	Carbon Number Applicability Range	Notes
TM1	Flash Vapor	Baseline; tight-line flash recombination
TM2	GPA 2177; ASTM D7900; ASTM D7169	All GC methods
TM3	Flash V; ASTM D8003; ASTM D7169	Built around HPLIS
TM4		
TM5		

N2 CO2 C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30

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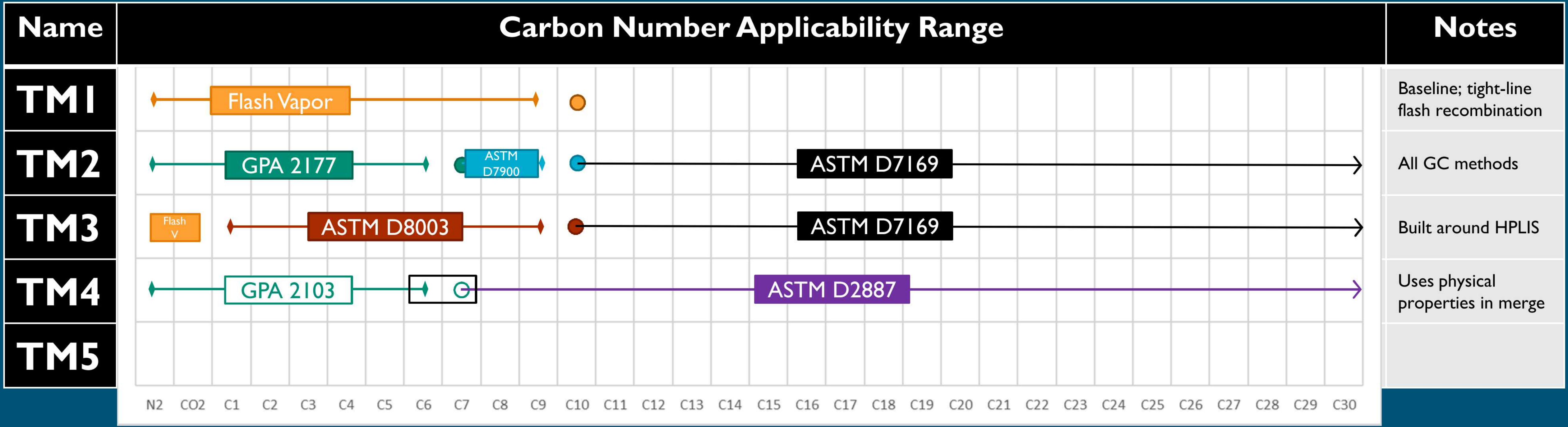

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TM3	Flash V; ASTM D8003; ASTM D7169	Built around HPLIS
TM4	GPA 2103; ASTM D2887	Uses physical properties in merge
TM5	Stabilized sample; Loss of light ends; ASTM D7900; ASTM D7169	DHA+HTSD

N2 CO2 C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30

- the carbon number associated with the residual for a given single method

- high measurement uncertainty regions.

- physical property used in merge.

- residual fraction assumed to be accurate for a merge of two methods.

Compositional Methods

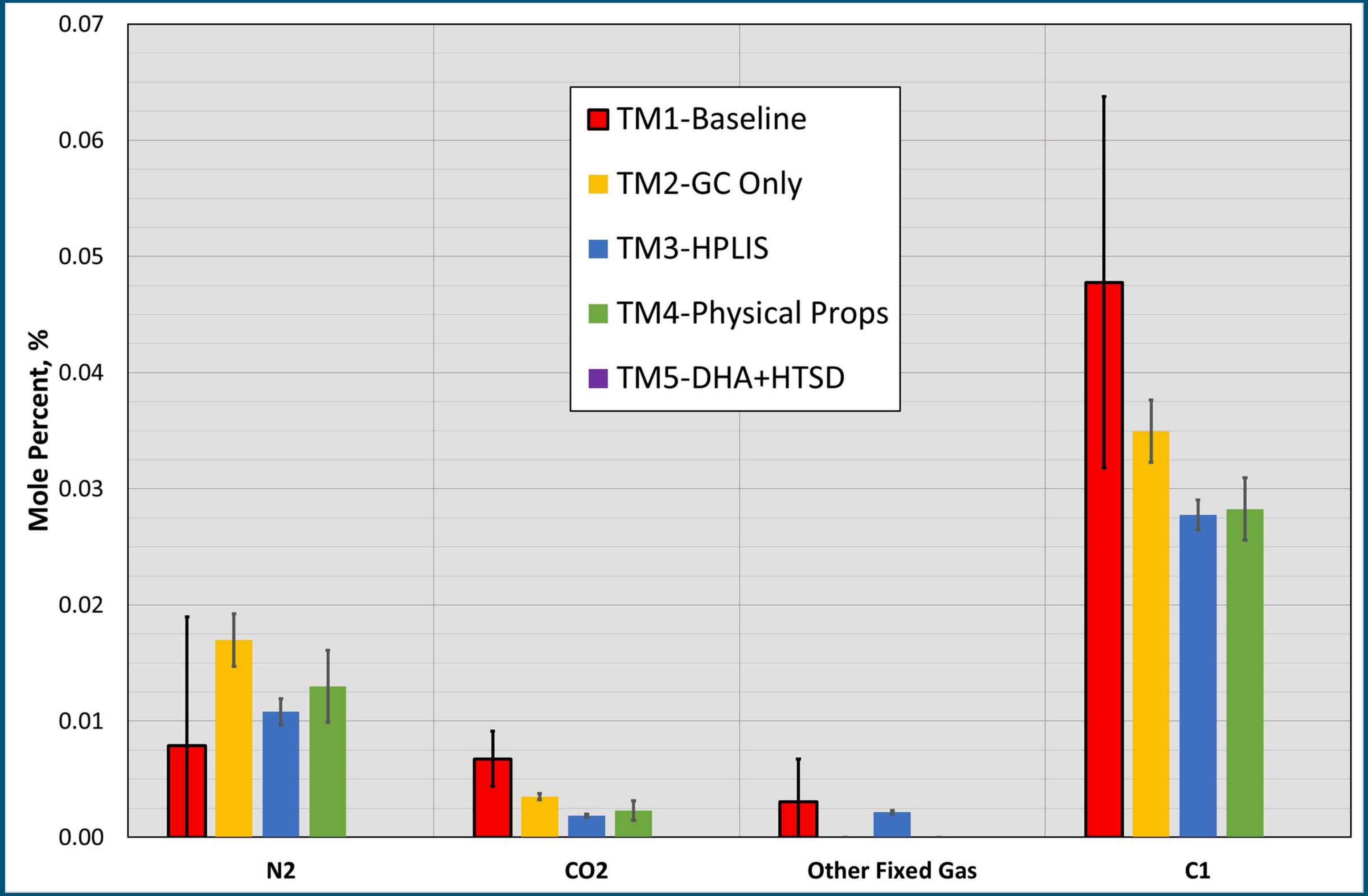
These methods were used to generate **compositional data** for **a conditioned North Dakota shale oil**.

Results

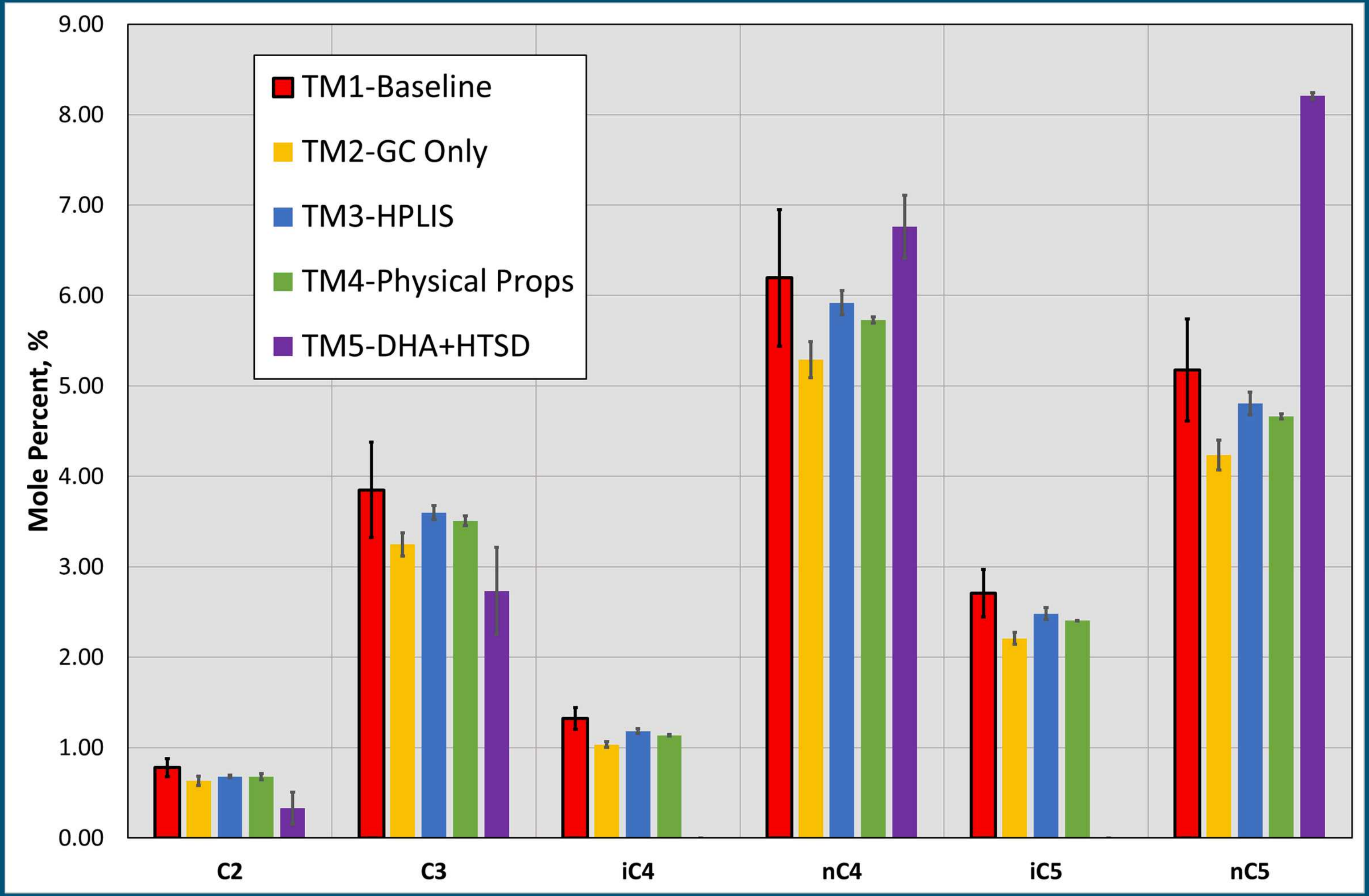
Compositional Results

Compare the results of the **various compositional analyses** for **light ends** that would affect VPCRx(100°F), V/L=0-4.

Compositional Results – Fixed Gases (N_2-C1)



Compositional Results – Light Ends (C2-C5)

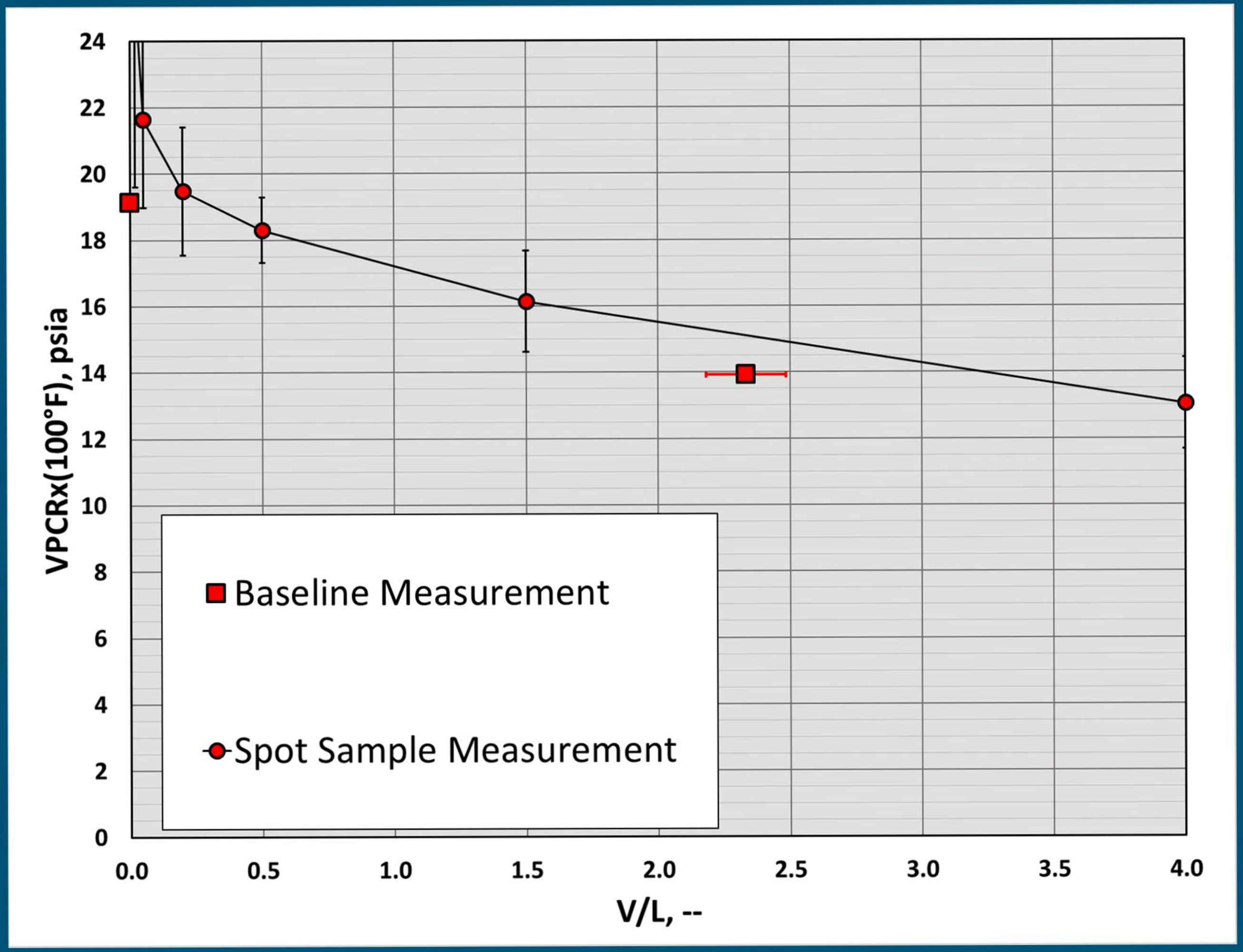


VPCRx Results

Compare the results of **EOS-calculated VPCRx(100°F)** to **baseline VPCRx(100°F)**.

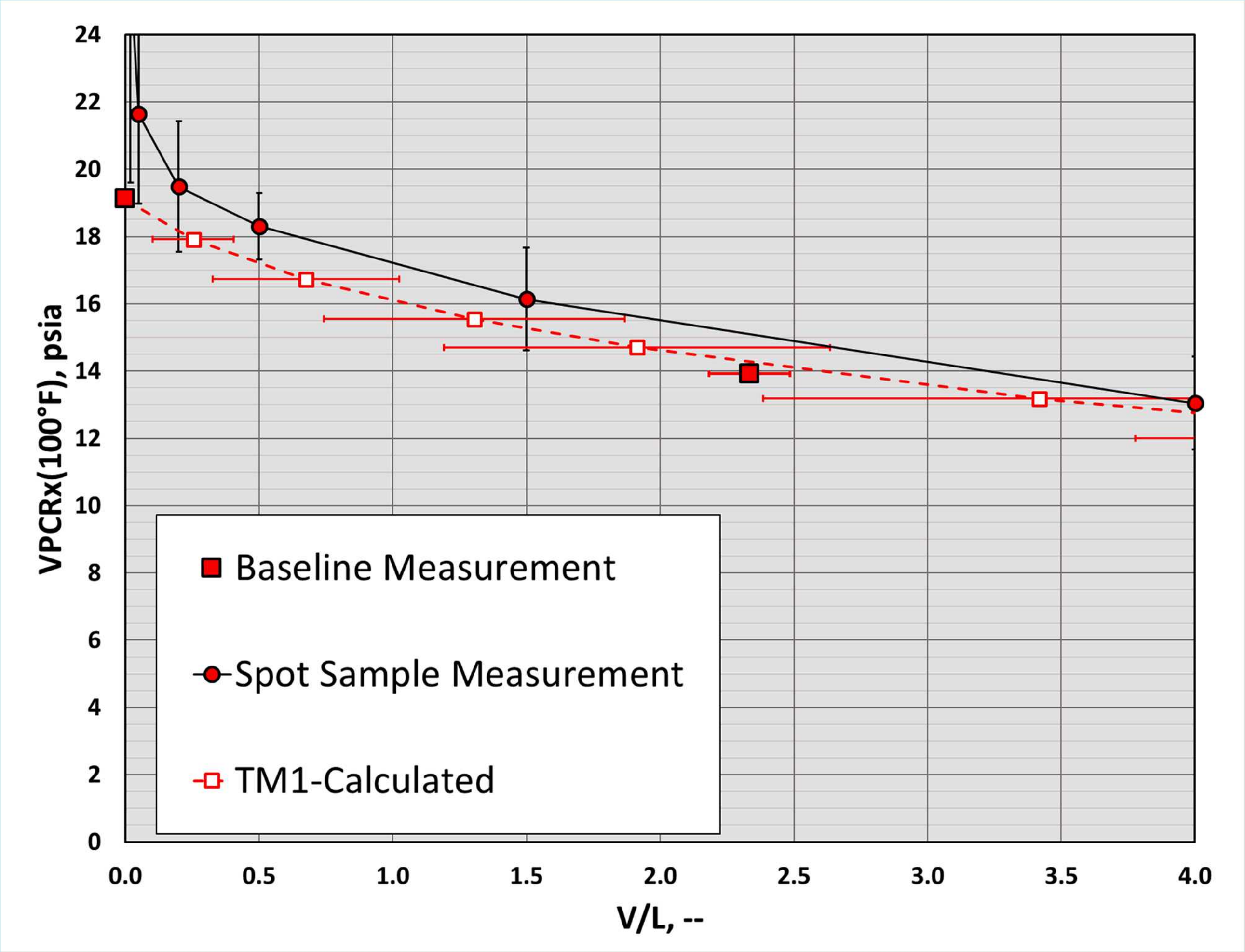
VPCRx Results

Direct measurements of VPCRx(100°F)



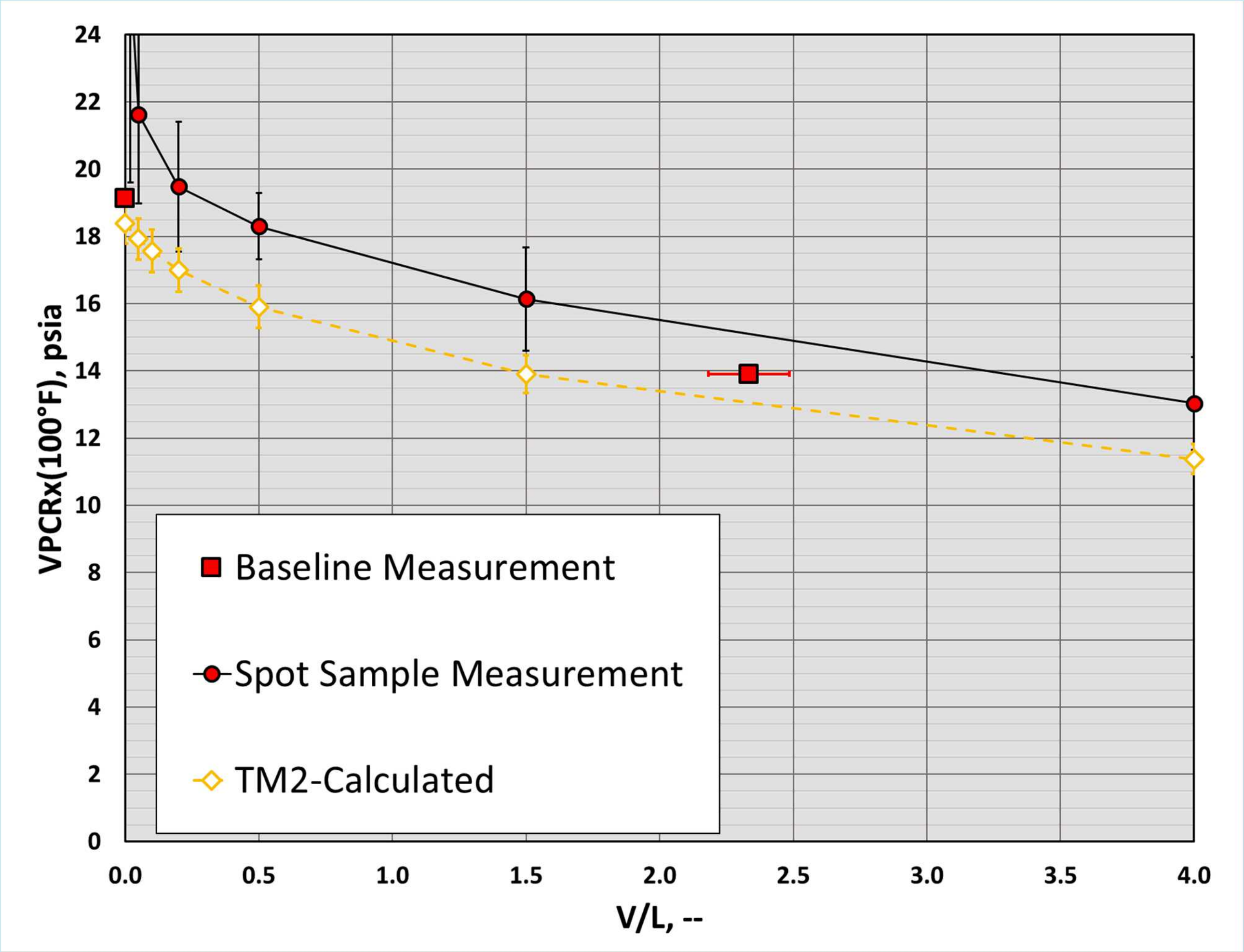
VPCRx Results

TM1 – Calculated VPCRx(100°F) using baseline composition



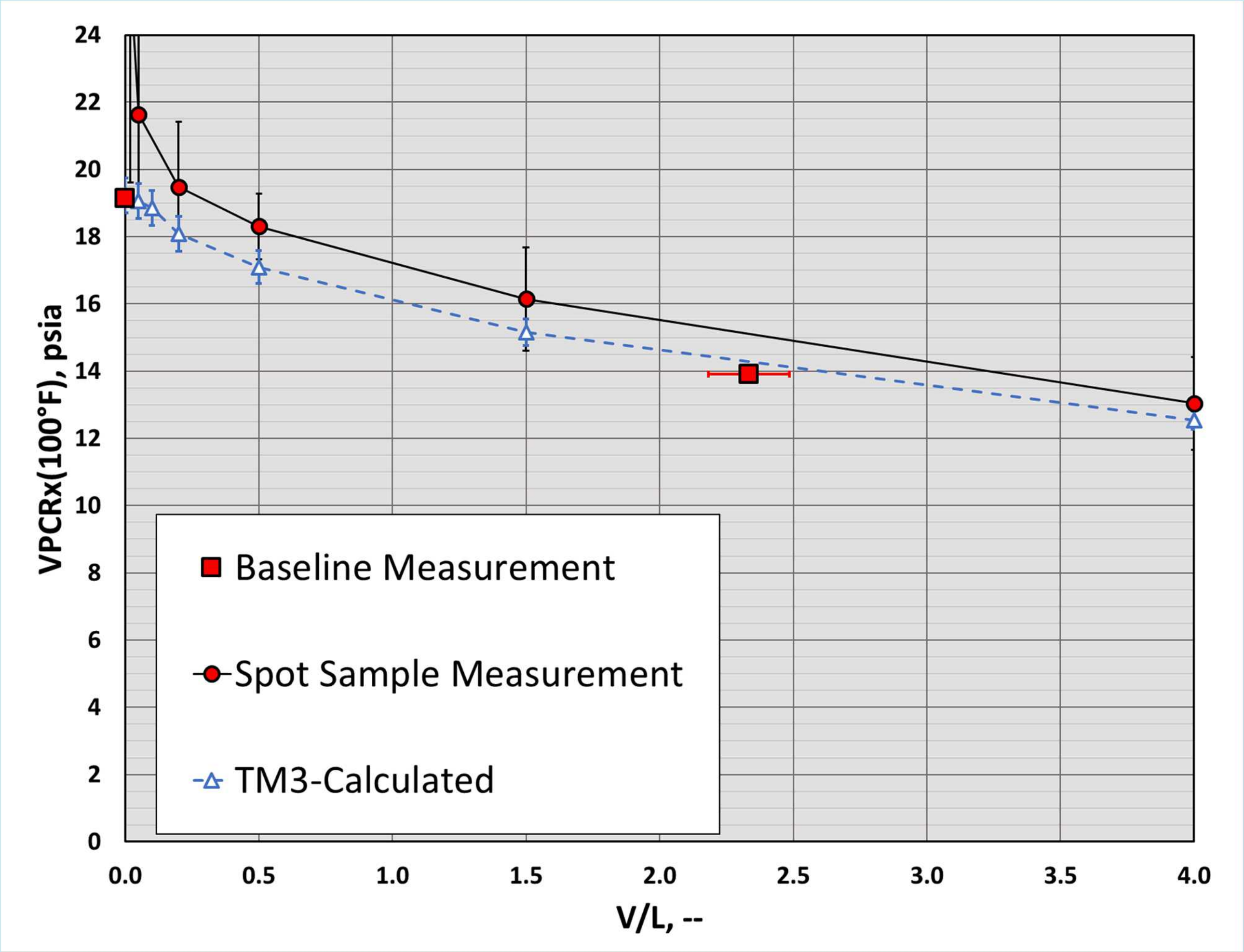
VPCRx Results

TM2 – Calculated VPCRx(100°F) using GC-only composition



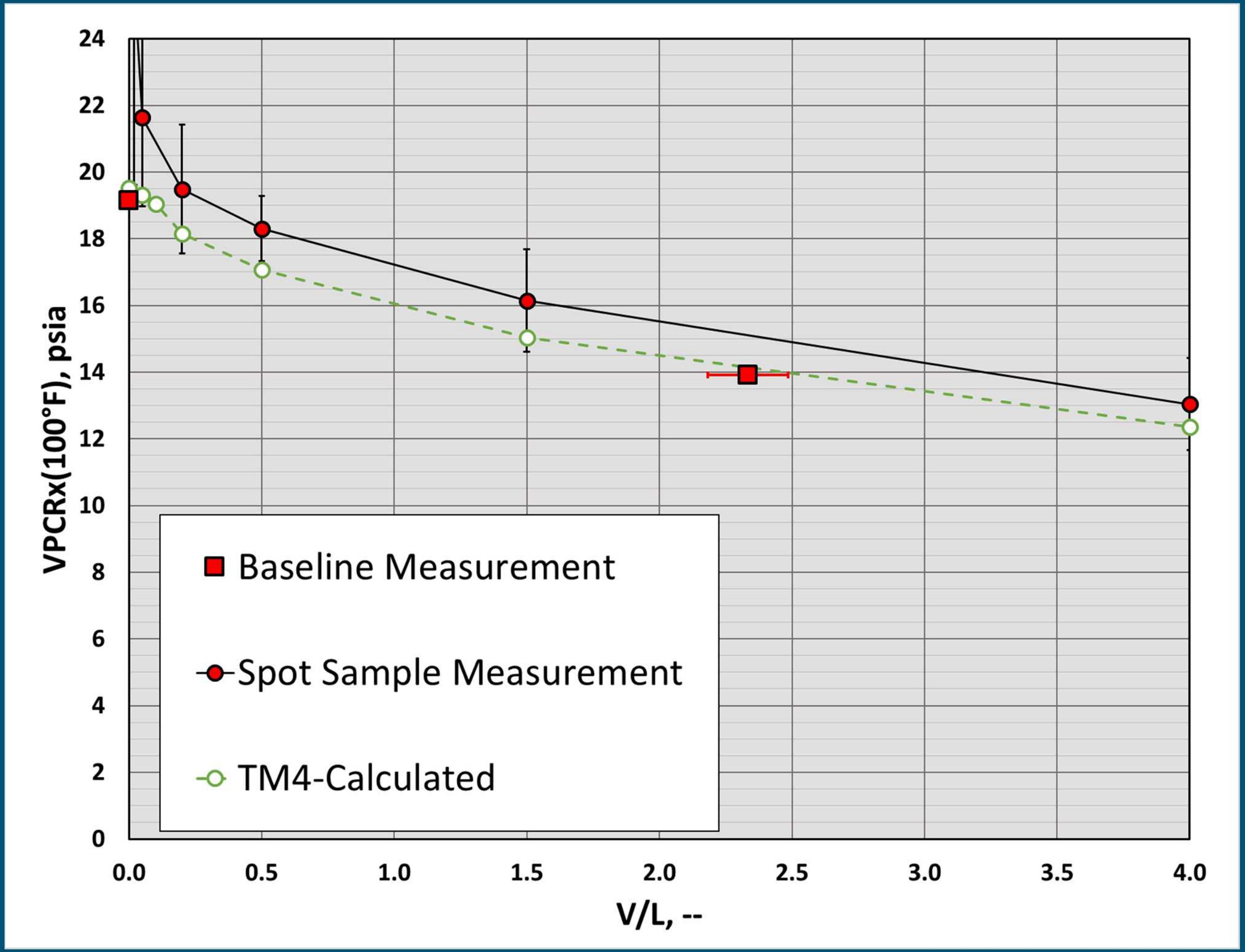
VPCRx Results

TM3 – Calculated VPCRx(100°F) using HPLIS+ composition



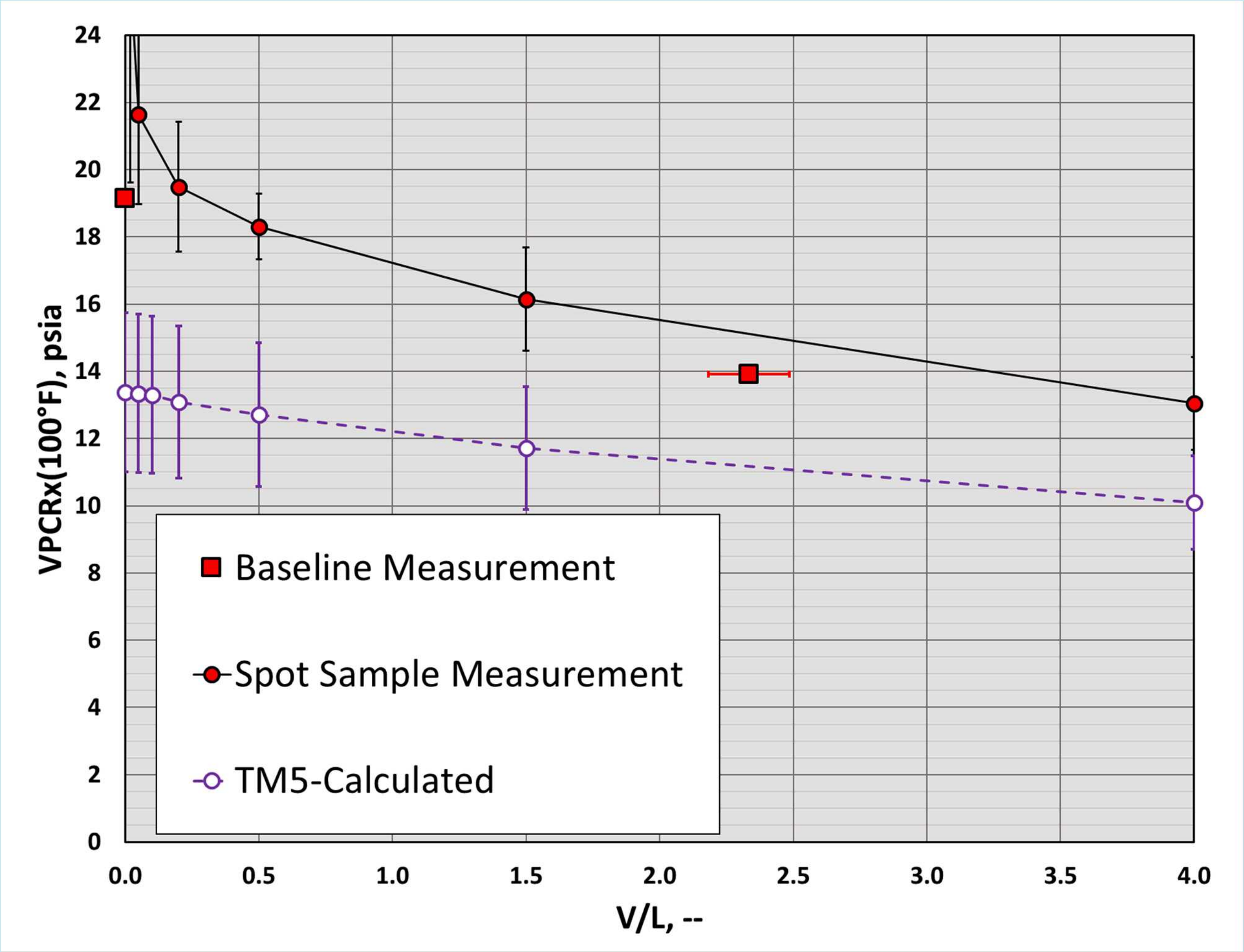
VPCRx Results

TM4 – Calculated VPCRx(100°F) using GC and physical properties composition



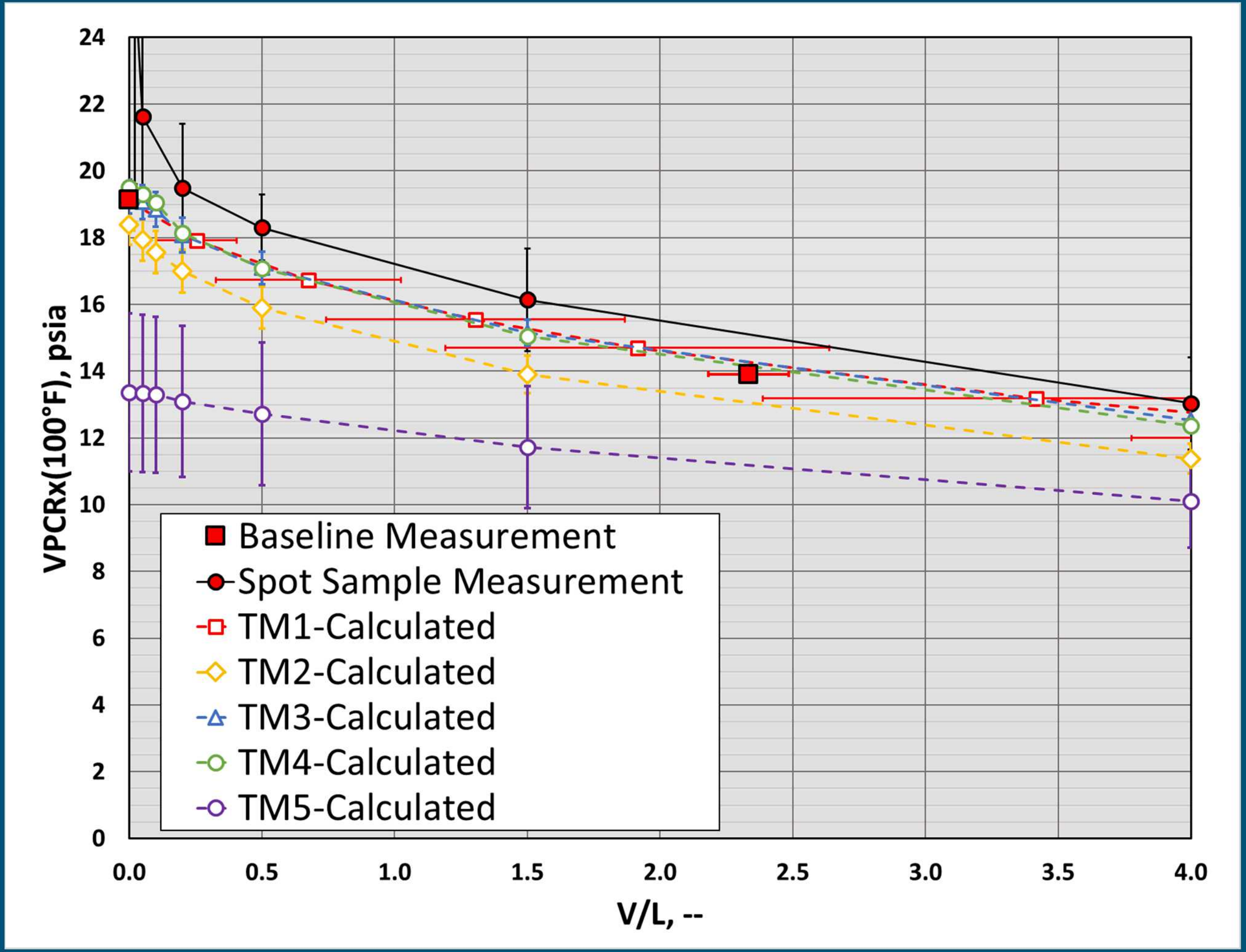
VPCRx Results

TM5 – Calculated VPCRx(100°F) using DHA+HTSD composition



VPCRx Results

Direct measurements of VPCRx(100°F)
TM1 – Calculated VPCRx using baseline composition
TM2 – Calculated VPCRx using GC-only composition
TM3 – Calculated VPCRx using HPLIS+ composition
TM4 – Calculated VPCRx using GC+physical properties composition
TM5 – Calculated VPCRx using DHA+HTSD composition



Conclusions

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- **Pressurized GC analysis + physical properties** can give compositions that produce VPCRx that are **consistent** with the baseline measurement for **conditioned shale oil**
  - TM3 – GPA 2103+GOR Merge+ASTM D2887
  - TM4 – GOR+ASTM D8003(HPLIS)+ASTM D7169(HTSD)

Conclusions

- **Pressurized GC analysis + physical properties** can give compositions that produce VPCRx that are **consistent** with the baseline measurement for **conditioned shale oil**
  - TM3 – GPA 2103+GOR Merge+ASTM D2887
  - TM4 – GOR+ASTM D8003(HPLIS)+ASTM D7169(HTSD)
- **Unpressurized GC analysis** can give compositions that produce VPCRx that are **not consistent** with the baseline measurement for **conditioned shale oil**
  - TM5 – ASTM D7900(DHA)+ASTM D7169(HTSD)

Conclusions

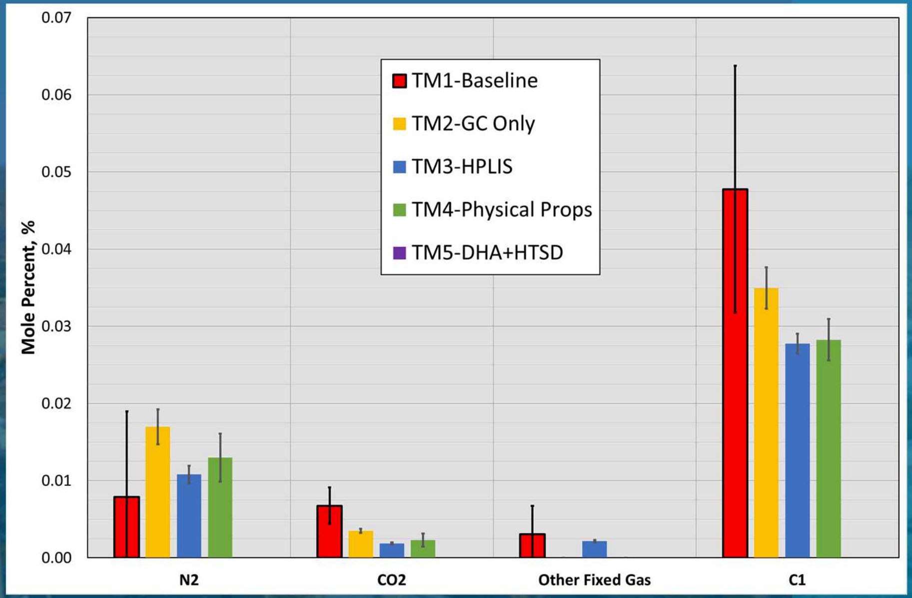
- **Pressurized GC analysis + physical properties** can give compositions that produce VPCRx that are **consistent** with the baseline measurement for **conditioned shale oil**
  - TM3 – GPA 2103+GOR Merge+ASTM D2887
  - TM4 – GOR+ASTM D8003(HPLIS)+ASTM D7169(HTSD)
- **Unpressurized GC analysis** can give compositions that produce VPCRx that are **not consistent** with the baseline measurement for **conditioned shale oil**
  - TM5 – ASTM D7900(DHA)+ASTM D7169(HTSD)
- **GC-only analysis** was mediocre in this case
  - TM2 – GPA 2177+ASTM D7900(DHA)+ASTM D7169(HTSD)

Publications

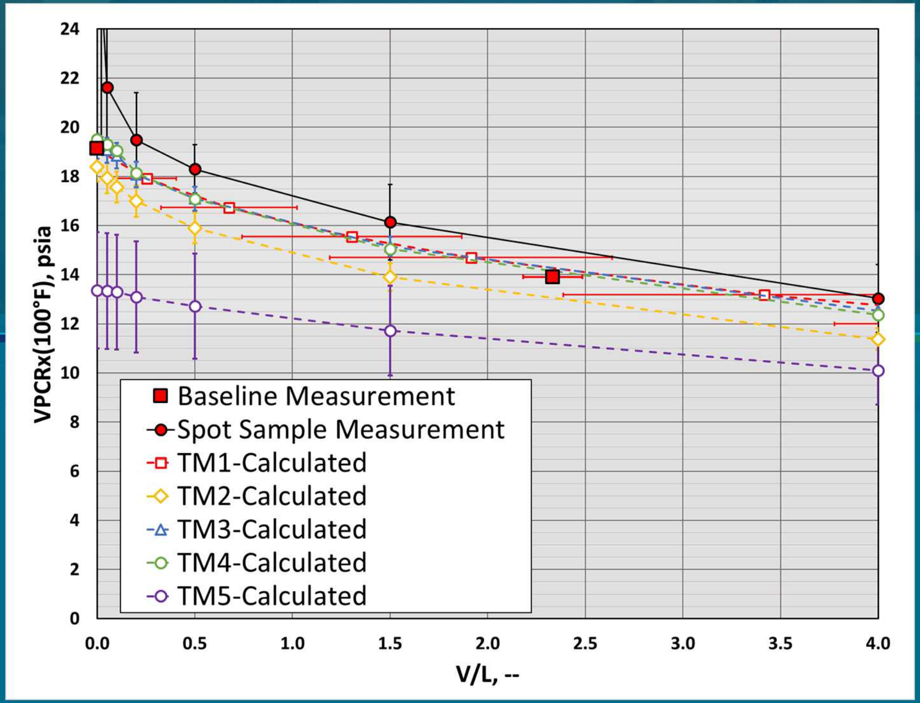
Lord, D., A. Luketa, C. Wocken, S. Schlasner, R. Allen and D. Rudeen (2015). "Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport." Unclassified Unlimited Release **SAND2015-1823**. Sandia National Laboratories, Albuquerque, NM.

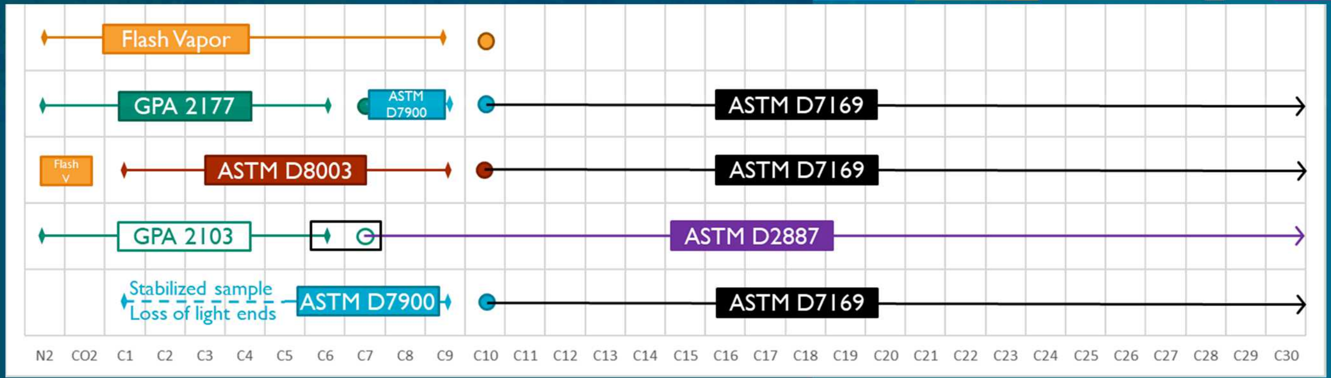
Lord, D., R. Allen, D. Rudeen, C. Wocken and T. Aulich (2018). "DOE/DOT Crude Oil Characterization Research Study, Task 2 Test Report on Evaluating Crude Oil Sampling and Analysis methods, Revision 1 - Winter Sampling." Unclassified Unlimited Release **SAND2018-5909**. Sandia National Laboratories, Albuquerque, NM.

Hogge, J.W., D. Lord, R. Allen, and D. Rudeen (2019). "Crude Oil Spot Sampling Methods and Their Impact on Thermophysical Properties." in AIChE Annual Meetings, 2019. Orlando, FL. Poster.


TM1-Baseline
TM2-GC Only
TM3-HPLIS
TM4-Physical Props
TM5-DHA+HTSD
Mole Percent, %
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
N2
CO2
Other Fixed Gas
C1

Thank you.


Baseline Measurement
Spot Sample Measurement
TM1-Calculated
TM2-Calculated
TM3-Calculated
TM4-Calculated
TM5-Calculated
VPCRx(100°F), psia
V/L, --
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


Flash Vapor
GPA 2177
ASTM D7900
ASTM D7169
Flash V
ASTM D8003
ASTM D7169
GPA 2103
ASTM D2887
Stabilized sample
Loss of light ends
ASTM D7900
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N2 CO2 C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30

Extra Slides

Acronyms

DHA – **Detailed Hydrocarbon Analysis**

EOS – **Equation of State**

GC – **Gas Chromatography**

HPLIS – **Heated Pressurized Liquid Injection System**

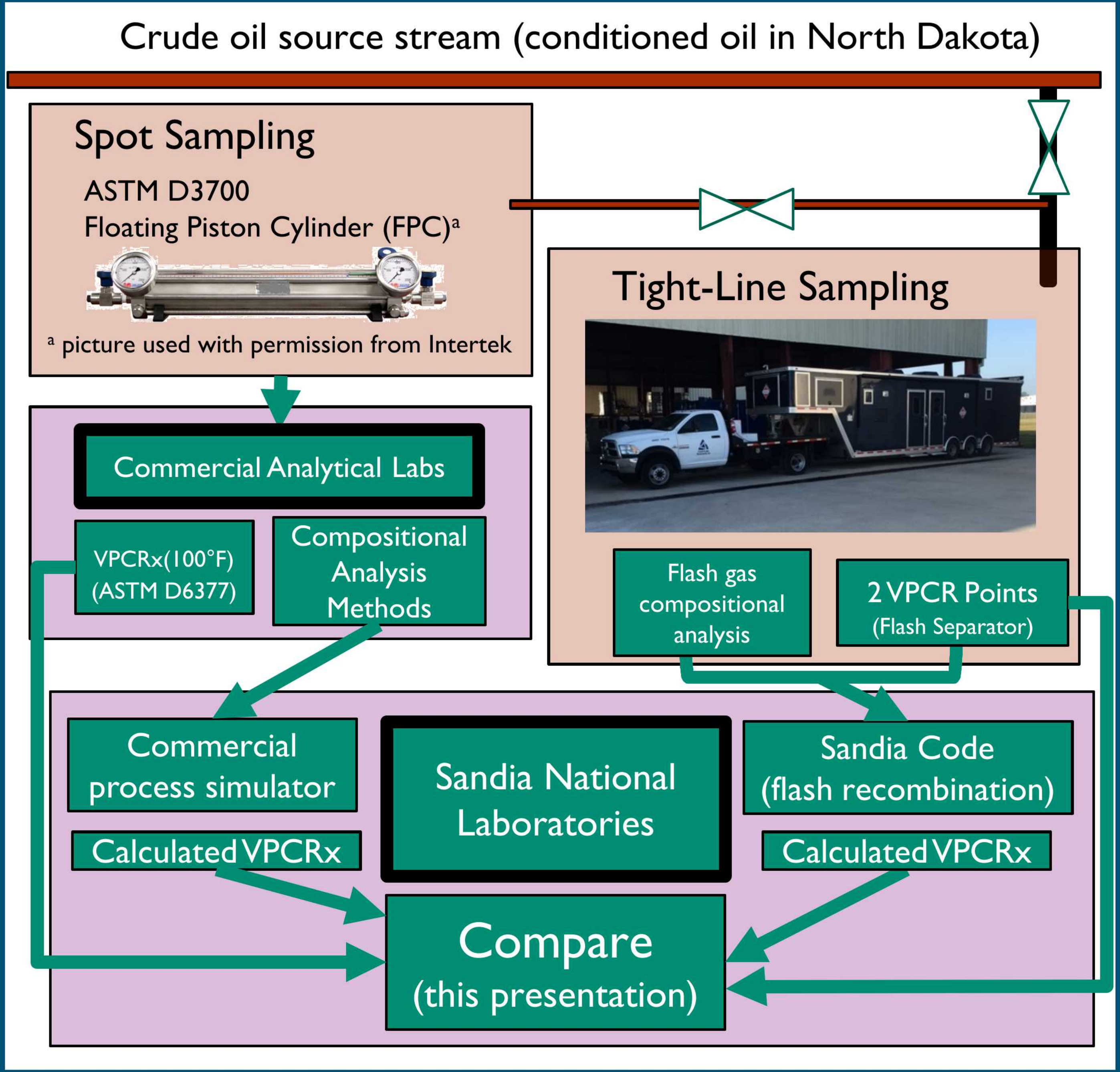
HTSD – **High Temperature Simulated Distillation**

V/L – **Vapor-to-Liquid volume ratio**

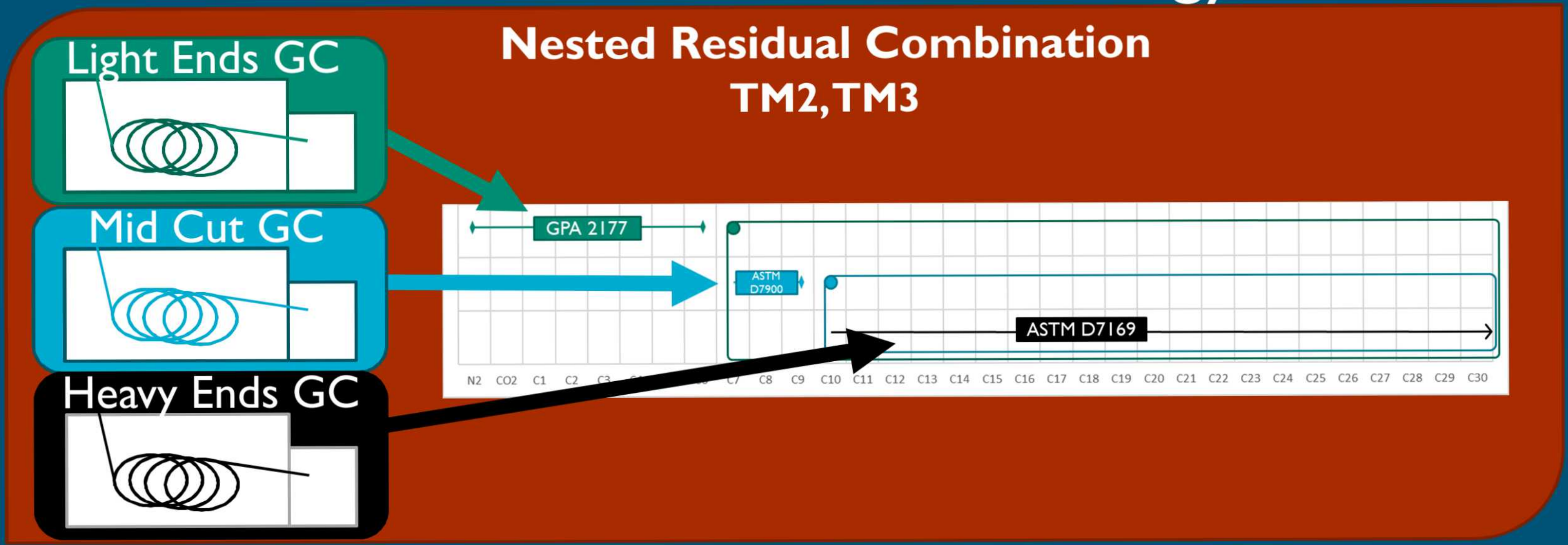
VPCRx – **Vapor Pressure of Crude at x=V/L**

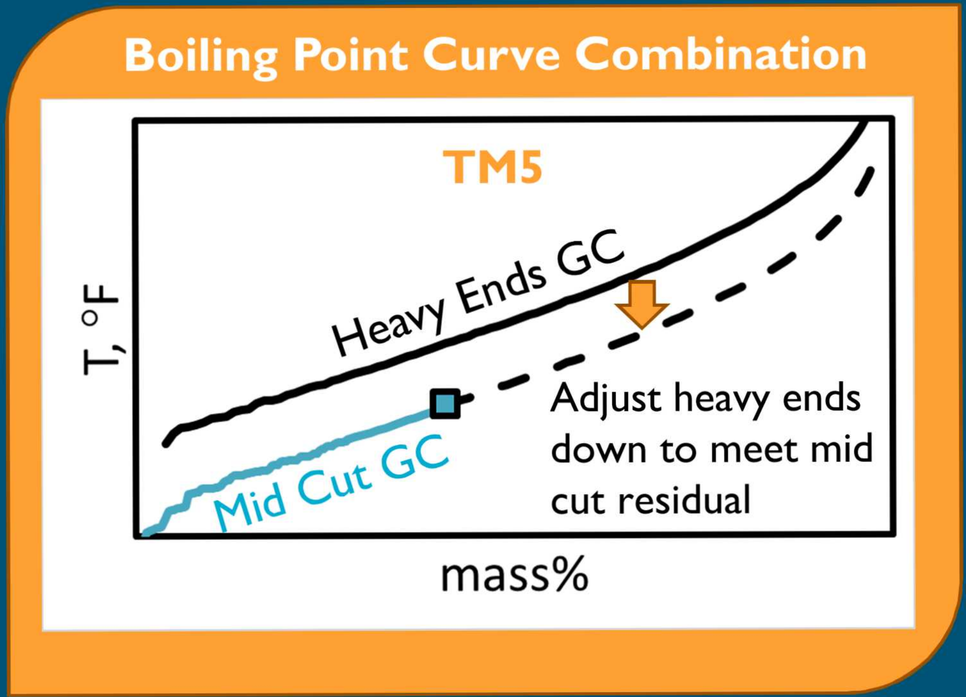
General Methods

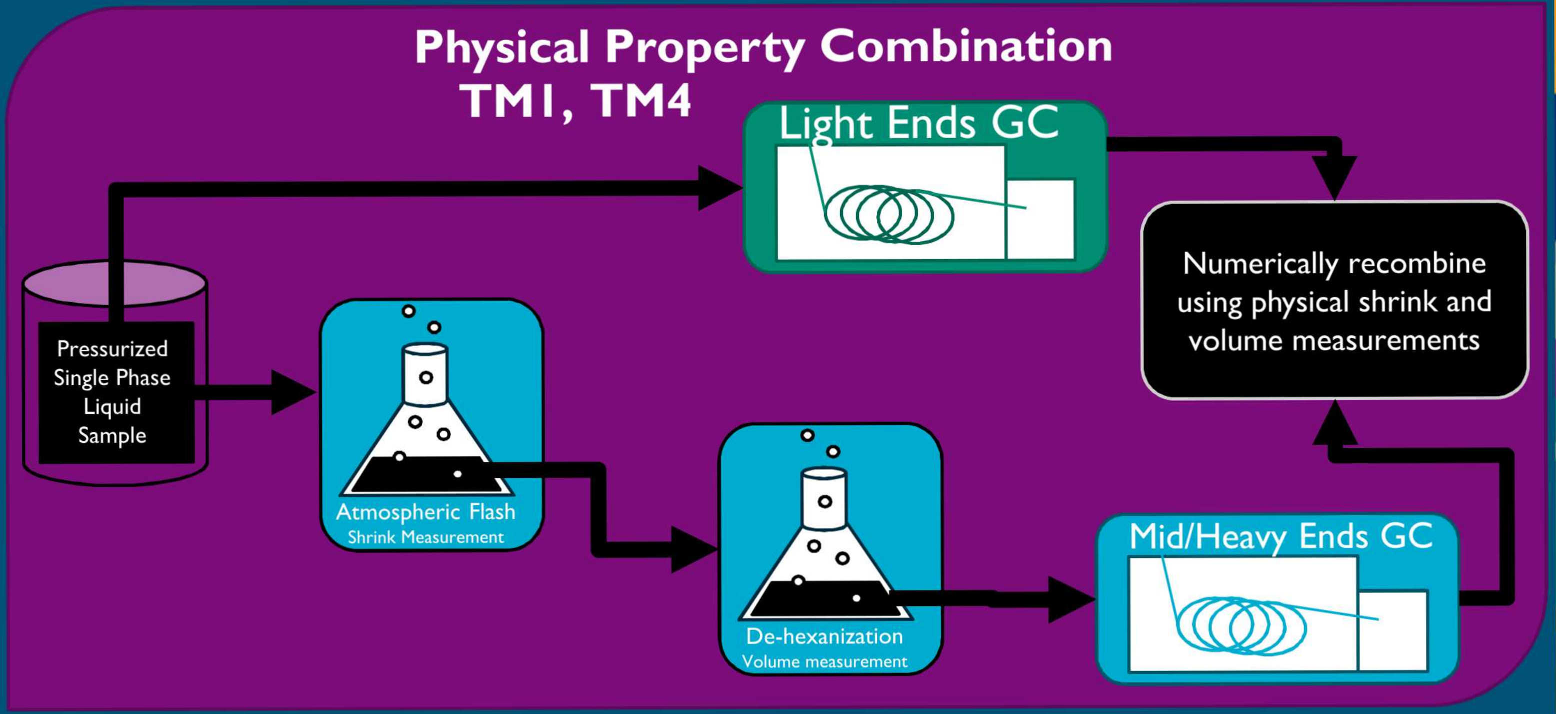
- Baseline – tight-line sampling/analysis method (expensive)
- Test methods – 1-L scale spot sampling, coupled with various commercially available analysis methods (less expensive)



Compositional Method – Combo Methodology







Discussion

- **Identify design needs** (what do I need to know?)
  - VPCRx(100°F), V/L=0-4 (measured and EOS-calculated)
- **Identify relevant properties** (what data do I need to know well?)
  - VPCRx (need a baseline for comparison)
  - Light ends composition (these affect EOS calculations of VPCRx at low V/L)
- **Identify methods that would provide sufficient quality data** (how should samples be taken? how should samples be analyzed?)
  - Closed 1-L spot sample (no loss of light ends during pressurized sampling)
  - Compositional analyses with:
    - Pressurized liquid injection into GC (TM3-HPLIS)
    - Physical properties used in data merge (TM4)

Used in next phase of Crude Oil Characterization Research Study