Live Crude Oil Volatility

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Vapour Pressure

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Light Ends Determination by GC

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ASTM Definition for Live Crude

- *Live crude oil,n* — crude oil with sufficiently high vapour pressure that it would boil if exposed to normal atmospheric pressure at room temperature.
- *Discussion* - Sampling and handling of live crude oils requires a pressurized sample system and pressurized sample containers to ensure sample integrity and prevent loss of volatile components.

Need – no method for Live Crude Oil

- ASTM D7169 HTSD
- Crude sample is diluted with CS_2 @ ambient temperature & pressure
- Light ends lost
- Light ends not reported
- Light ends are quenched by CS_2

Need – no method for Live Crude Oil

- ASTM D7900 Merge
- Internal Standard is added to crude sample at ambient Temperature & Pressure
- Light ends lost
- Light ends are reported (usually to nC10 DHA) and remainder of crude is backflushed
- Data is then used to correct CS_2 quenching in distillation curve by mathematically “merging” with D7169

Need – no method for Live Crude Oil

- ASTM D7900 / ASTM D7169
- Samples are collected under atmospheric conditions
- Use of sealed sample collection cylinders not mentioned

Sampling

Sealed container (D3700 FPC) or D1265 cylinder required

API/ASTM also working on MPC

Bakken.mp4

ENVANTAGE INCORPORATED

Safety & Economic Drivers

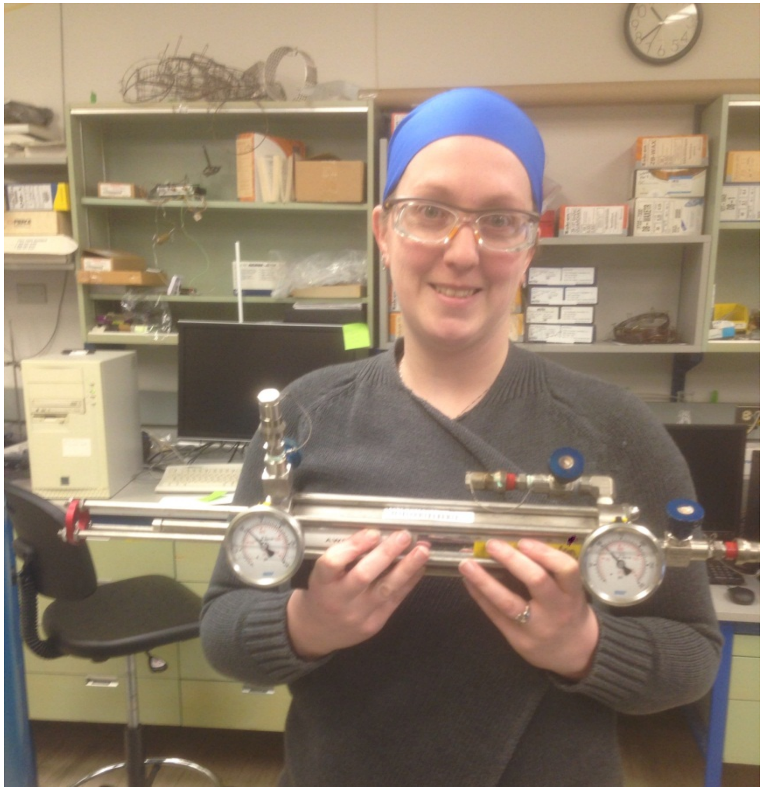
- Transportation
  - Rail cars
- Crude Oil Valuation
  - Custody transfer
  - Refinery impacts
  - Compliance

High Vapour Pressure Live Crude Oil

- Analysis Issues
  - Sampling
    - API/ASTM manual piston cylinder sampling practice currently on D02 main
  - Vapour Pressure
    - Direct analysis of TVP via field method ASTM D7975 and ASTM D6377 lab method vs RVP ASTM D323
    - Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCRx-F(Tm°C) (Manual Expansion Field Method)
  - Light end composition
    - HPLIS/GC with EOS TVP calculations

Sampling

- pressurized samples - cylinders
  - ASTM D3700 Floating Piston Cylinder or ASTM D1265 LPG type with ullage



ASTM D8003 Scope

- This test method covers the determination of light hydrocarbons and cut point intervals via gas chromatography in live crude oils and condensates with $VPCR_4$ up to 500 kPa at 37.8 °C as described in Test Method D6377
- Methane (nC_1) to hexane (nC_6) including iC5, benzene, and benzene precursors are speciated and quantitated.

HPLIS Method Summary

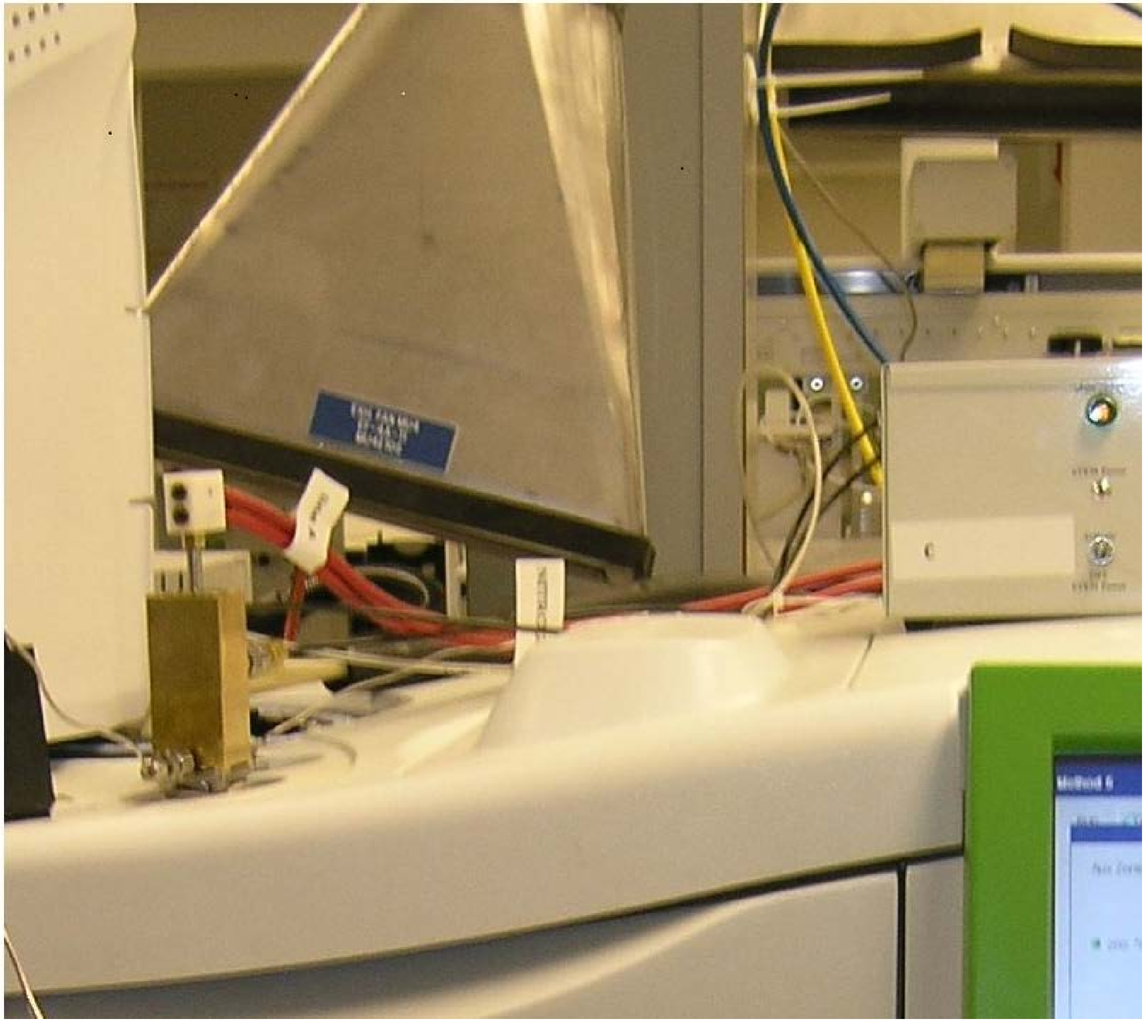
- Liquid sample valve connected to pressurized sample
- Theoretical mass response factors
- Cut point fractions – generalized physical properties
- External std calibration with density correction – determination of residue – similar to RGO in D7169
- Primary purpose is light end quant – BP distribution can be determined

Component	Molecular Weight of Component (g/mol)	Density of Component @ 20 °C (g/mL)	Generalized Boiling Point of Cut Point Fraction Interval °C	Generalized Molecular Weight of Cut Point Fraction Interval (g/mol)	Generalized Density of Cut Point Fraction Interval @ 20 °C (g/mL)	Theoretical Mass Response Factor
C1	16.04	0.36				1.00
C2	30.08	0.45				0.937
C3	44.01	0.52				0.916
iC4	58.12	0.549				0.906
n-C4	58.12	0.5788				0.906
iC5	72.15	0.6201				0.899
n-C5	72.15	0.6262				0.899
n-C6	86.18	0.6603	63.9	84	0.685	0.895
Benzene	78.12	0.8765				0.812
n-C7	100.21	0.6837	91.9	96	0.722	0.892
n-C8	114.23	0.7025	116.7	107	0.745	0.890
n-C9	128.76	0.7176	142.2	121	0.764	0.888
n-C10	142.29	0.73	165.8	134	0.778	0.887
n-C11	156.32	0.7402	187.2	147	0.789	0.886
n-C12	170.34	0.7487	208.3	161	0.800	0.885
n-C13	184.37	0.7564	227.2	175	0.811	0.884
n-C14	198.4	0.7628	246.4	190	0.822	0.883
n-C15	212.42	0.7685	266	206	0.832	0.883
n-C16	226.45	0.7733	283	222	0.839	0.882
n-C17	240.48	0.778	300	237	0.847	0.882
n-C18	254.51	0.782	313	251	0.852	0.881
n-C19	268.53	0.7855	325	263	0.857	0.881
n-C20	282.56	0.7886	338	275	0.862	0.881
n-C21	296.59	0.7919	351	291	0.867	0.880
n-C22	310.61	0.7944	363	305	0.872	0.880
n-C23	324.67	0.7969	375	318	0.877	0.880
n-C24	338.67	0.7991	386	331	0.881	0.880
Residue			540	500	0.925	0.88

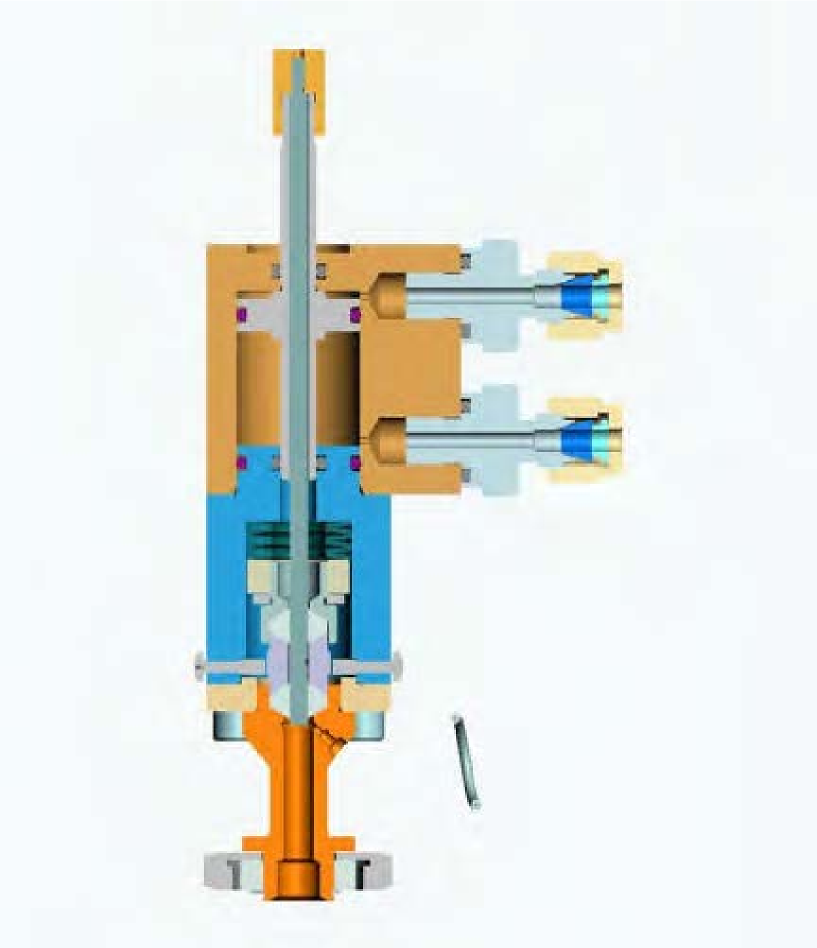
Instrument Set-up

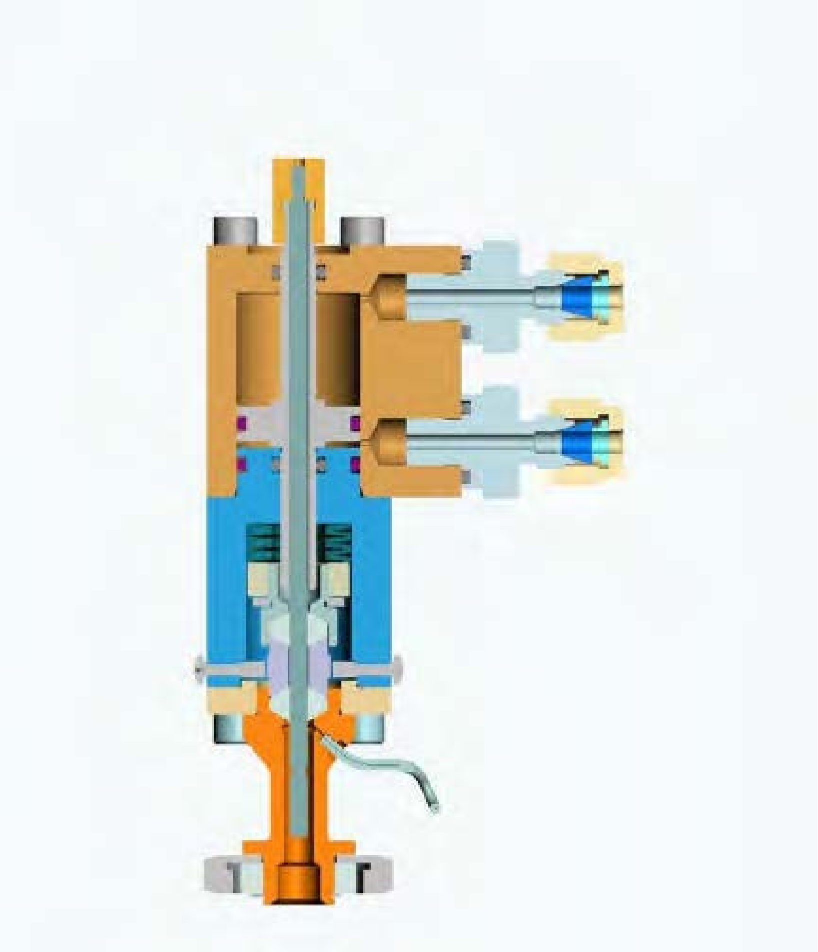
- Hydrogen Carrier GC
- HPLIS – heated stem injection (200°C)
- Split/splitless injector
- MXT1 15m x 0.280mm, 3um film column.
- FID detector

HPLIS valve on GC

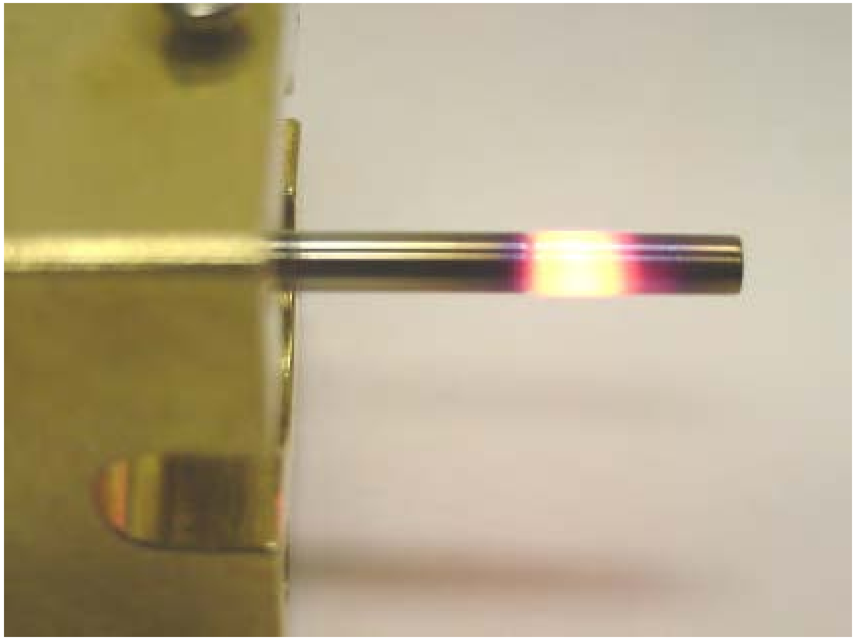


HPLIS Load and Inject Positions

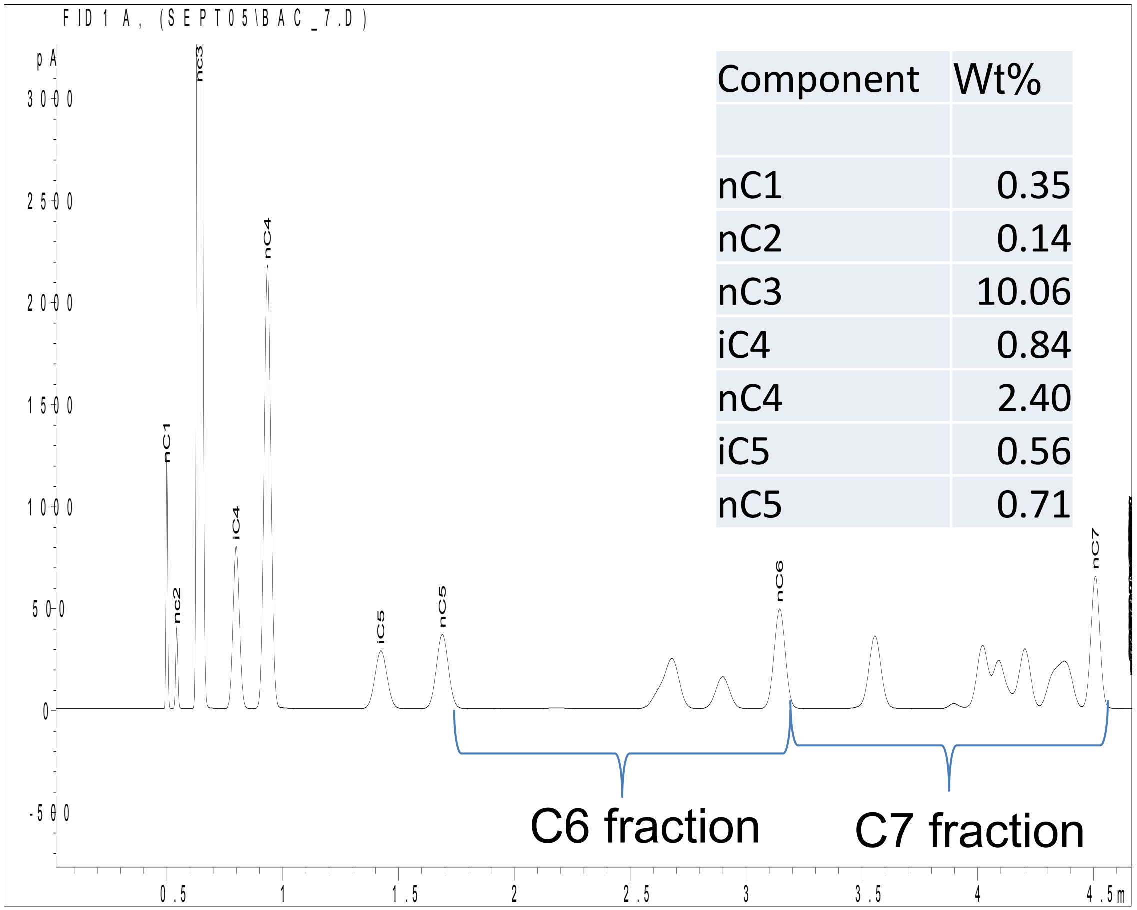




Heated STEM of HPLIS

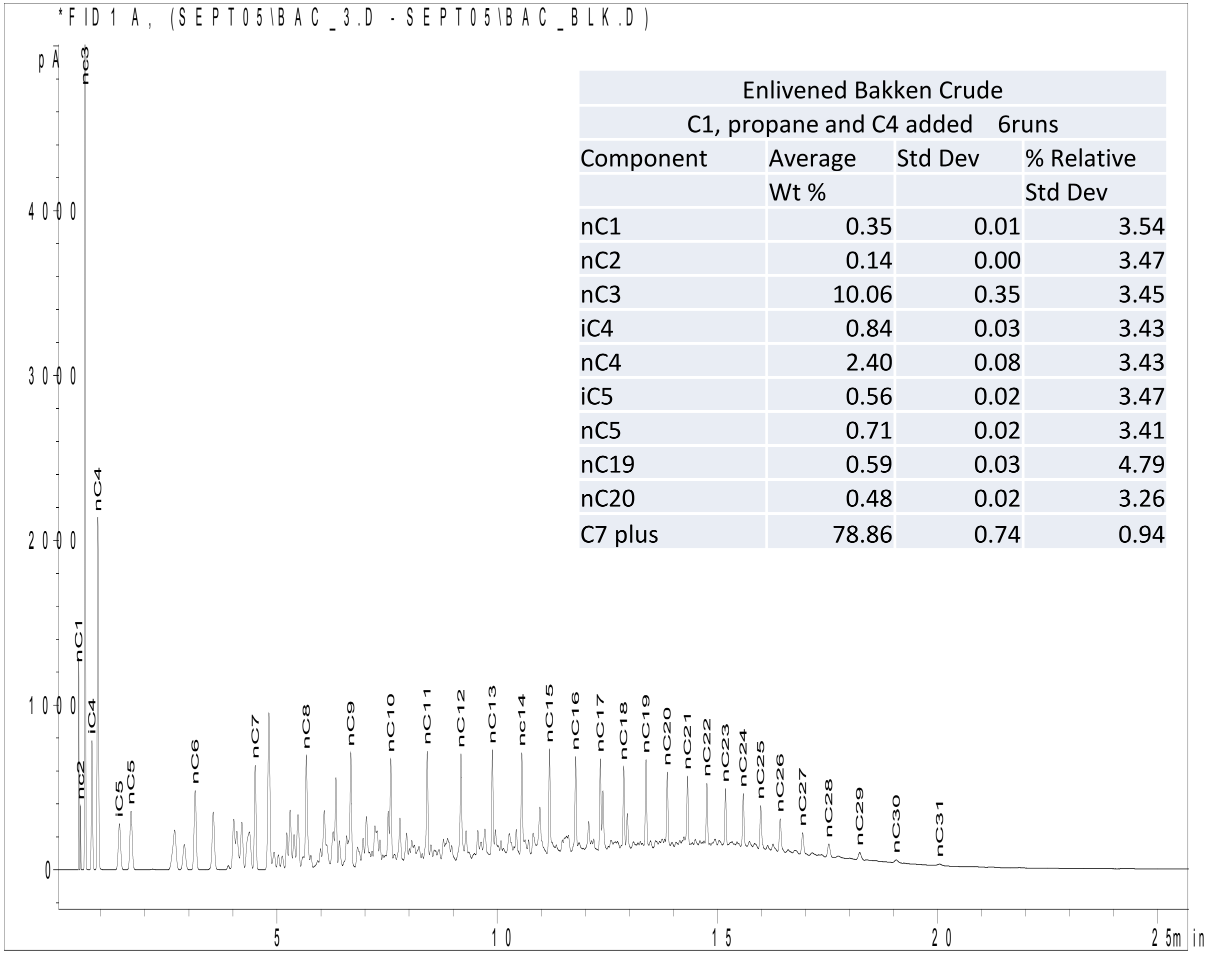


C1-C7 peaks resolution



Component	Wt%
nC1	0.35
nC2	0.14
nC3	10.06
iC4	0.84
nC4	2.40
iC5	0.56
nC5	0.71

Enlivened Bakken Crude



Enlivened Bakken Crude			
C1, propane and C4 added 6runs			
Component	Average Wt %	Std Dev	% Relative Std Dev
nC1	0.35	0.01	3.54
nC2	0.14	0.00	3.47
nC3	10.06	0.35	3.45
iC4	0.84	0.03	3.43
nC4	2.40	0.08	3.43
iC5	0.56	0.02	3.47
nC5	0.71	0.02	3.41
nC19	0.59	0.03	4.79
nC20	0.48	0.02	3.26
C7 plus	78.86	0.74	0.94

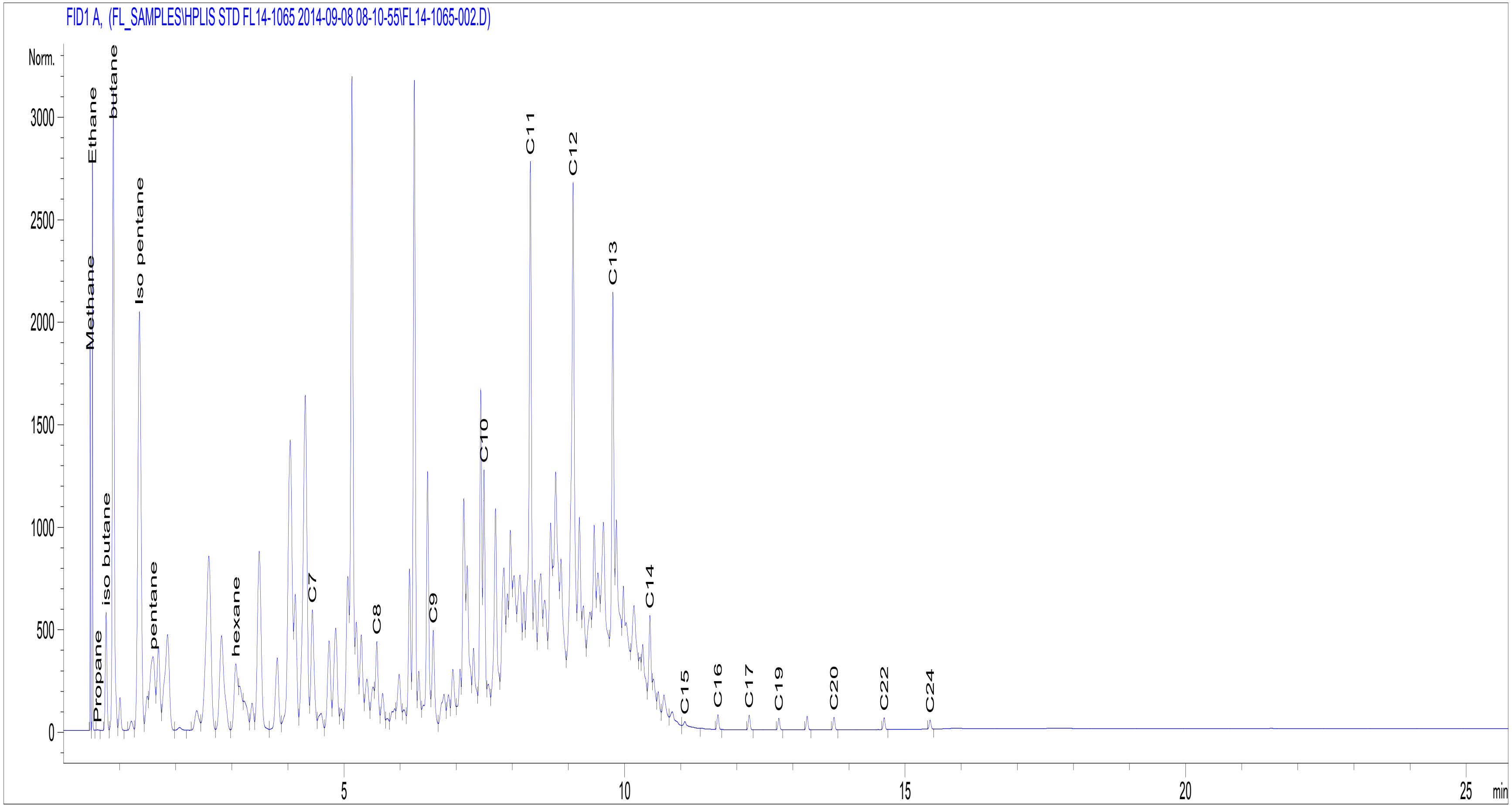
Calibration Standards

- Gasoline/Jet A1mix spiked with methane, ethane, and n-paraffin's betweenC16 and C24.
- Seven D1265 cylinders were made and run multiple times on the HPLIS to get precision data, and verify the ability to make homogeneous samples in cylinders of this type.

Calibration Standard 7 cylinders -24 runs

	Average, mass%	StdDev	Max	Min	r estimate	%RSD
Methane	0.156	0.0075	0.175	0.137	0.0208	4.8
Ethane	0.546	0.0179	0.585	0.478	0.0496	3.3
Propane	0.002	0.0001	0.002	0.002	0.0003	4.6
Isobutane	0.448	0.0103	0.458	0.404	0.0285	2.3
Butane	2.769	0.0588	2.829	2.515	0.1629	2.1
C4+ to C17-	95.759	0.0893	96.134	95.633	0.2474	0.1
c17	0.063	0.0006	0.064	0.062	0.0017	1.0
c18	0.050	0.0005	0.051	0.049	0.0014	1.0
c19	0.058	0.0006	0.059	0.057	0.0017	1.0
c20	0.055	0.0007	0.057	0.054	0.0019	1.2
c22	0.052	0.0010	0.055	0.051	0.0028	2.0
c24	0.041	0.0019	0.047	0.038	0.0053	4.7
TOTAL AREA	210094	5286	222713	203066		2.5

Calibration Standard



Validation standards – accumulator (FPC)

Five samples prepared from a dead oil, with different target mass% concentrations of light ends.

		C1	C2	C3	iC4	nC4	iC 5	nC5	nC6	Sample VP (kPa) at 4:1 Vapour-to-liquid volume ratio at 37.8°C
Sample 1	High	0.25	0.75	0.5	0	0	1	5	8	174
Sample 2	Typical	0.05	0.25	1.5	0	3.7	1	2.9	4	128.7
Sample 3	typical repeat	0.05	0.25	1.5	0	3.7	1	2.9	4	128.7
Sample 4	typical high c1,c2,c3	0.1	0.5	3	0	0	1	2.9	4	183.7
Sample 5	Low sample	0.05	0.075	0	0	15	0	0	0	Not calculated

Dead Oil Analysis

Component/Cut Point	HPLIS GC, mass%
METHANE	0.00
ETHANE	0.00
PROPANE	0.00
IC4	0.00
NC4	0.00
IC5	0.00
NC5	0.00
C6's	0.00
C7	0.14
C8	1.18
C9	2.89
C10	4.65
C10+	91.14
Total	100

Subsequent slides show pure component spikes into the dead oil (except for C6 "hexanes" was used).

NOTE: C6 isomers eluting after nC6 are included in the C7 Cut Point Fraction (Slide 19) Therefore total of C6 and C7 fractions are presented for comparison

Sample 1

Component/Cut	HPLIS GC, mass%	Actual, mass%
METHANE	0.25	0.29
ETHANE	0.74	0.87
PROPANE	0.54	0.59
IC4	0.00	0.00
NC4	0.00	0.00
IC5	0.96	1.02
C5	4.64	4.99
C6	6.18	7.98
C7 (includes C6 isomers)	1.46	0.12
C6's + C7	7.64	8.10
C8	1.08	0.99
C9	2.51	2.44
C10	4.00	3.92
NC10+	77.64	76.80
Total	100	100

Sample 2 & 3

Components	HPLIS GC	Actual	HPLIS GC	Actual
METHANE	0.05	0.06	0.05	0.06
ETHANE	0.18	0.29	0.10	0.29
PROPANE	1.46	1.47	1.34	1.51
IC4	0.01	0.00	0.01	0.00
NC4	3.63	3.88	3.41	3.87
IC5	0.92	1.01	0.92	1.00
NC5	2.68	2.92	2.72	3.00
C6	3.10	4.01	3.30	3.98
C7 (includes C6 isomers)	0.80	0.12	0.83	0.12
C6 + C7	3.90	4.13	4.13	4.10
C8	1.10	1.02	1.06	1.02
C9	2.57	2.50	2.54	2.50
C10	4.14	4.02	4.05	4.01
C10+	79.37	78.71	79.66	78.65
Total	**100**	**100**	**100**	**100**

Sample 4

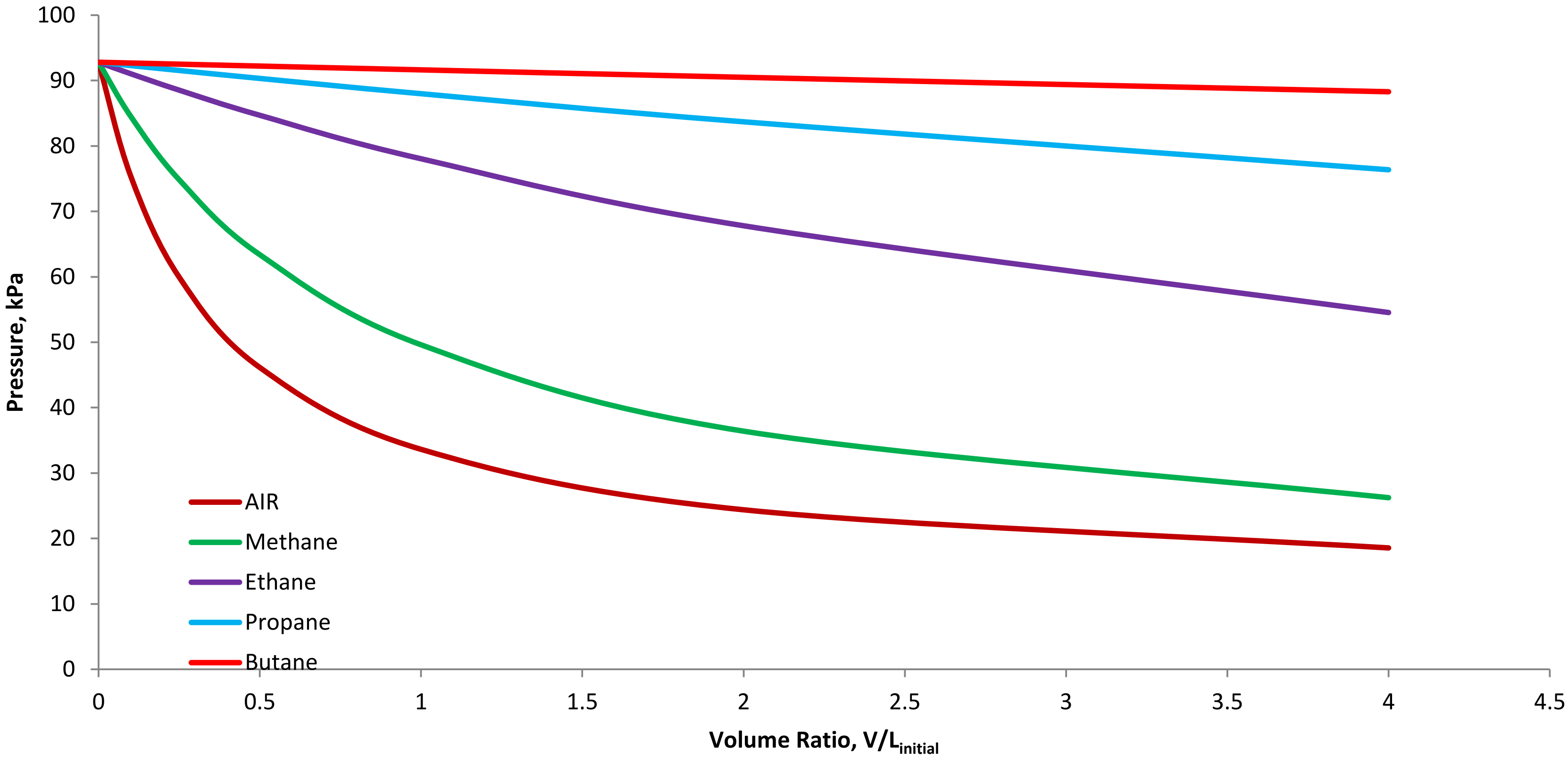
Component/Cut	HPLIS GC, mass%	Actual, mass%
METHANE	0.10	0.11
ETHANE	0.52	0.58
PROPANE	2.87	3.04
IC4	0.01	0.00
NC4	0.00	0.00
IC5	0.95	1.00
NC5	2.68	2.91
C6	3.13	3.98
C7 (includes C6 isomers)	0.80	0.12
C6 + C7	3.93	4.10
C8	1.12	1.04
C9	2.63	2.56
C10	4.28	4.11
C10+	80.90	80.55
Total	**100**	**100**

Sample 5

Component/Cut	HPLIS GC, mass%	Actual, mass%
METHANE	0.05	0.06
ETHANE	0.09	0.09
PROPANE	0.00	0.00
IC4	0.02	0.00
NC4	14.10	15.05
IC5	0.02	0.00
NC5	0.00	0.00
C6	0.00	0.00
C7 (includes C6 isomers)	0.13	0.12
C8	1.04	1.00
C9	2.54	2.45
C10	4.09	3.94
C10+	77.92	77.29
Total	**100.0**	**100.0**

EOS SRK Modeling of Binary Mixtures

- Calculated VP of gases in isooctane, 37.8C

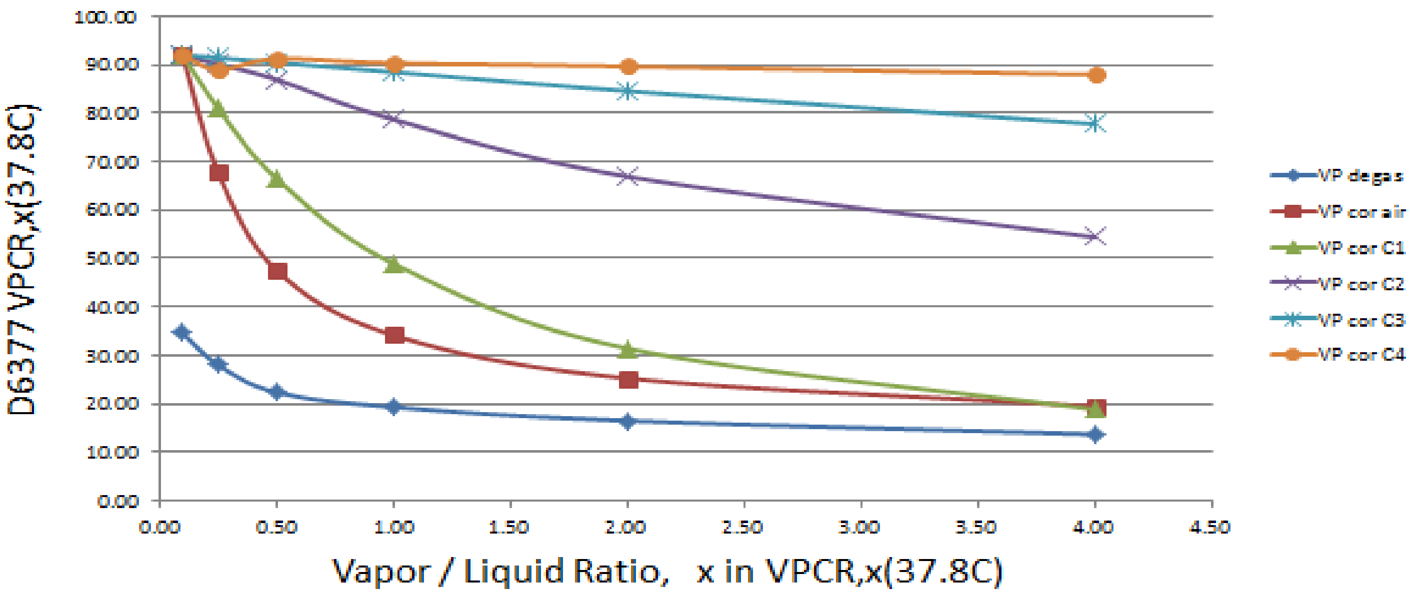


Experimental Values

Canadian Crude Quality Technical Association

2,2,4-Trimethylpentane Blend Comparison

- Difference between TVP and RVP is LARGE for Air, Methane and Ethane, SMALL for propane, butane and heavier
- Shape of the VP vs V/L curve can alert operator that an unknown sample received in the lab contains light dissolved gases



- Data for HC gases corrected for air content, and normalized to 92 kPa (barometric pressure at the time) at V/L = 0.1 to show relative contribution of light gases saturated in iC8 (224TMB) at 37.8C
- Samples prepared and analyzed at Alberta Innovates funded by CCQTA Executive Committee

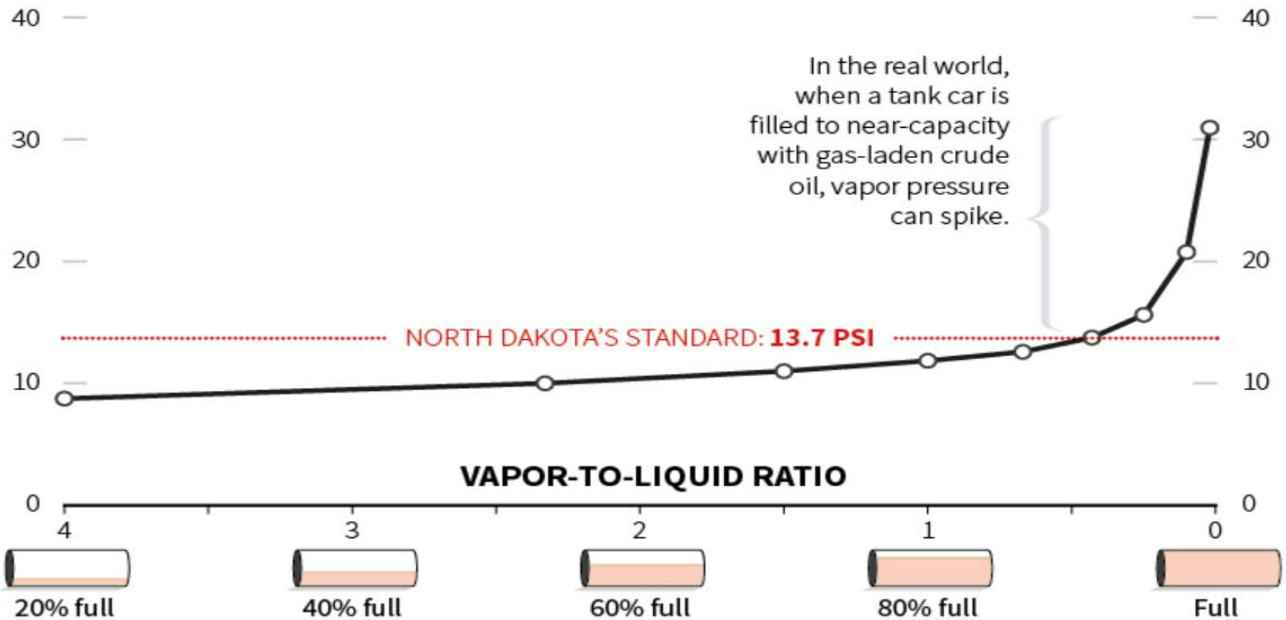
Reuters News Article

Vapor pressure in oil trains

North Dakota's standard will detect vapor pressure using a mostly-empty container but tank cars are practically fully-loaded when they move from field to refinery. Vapor pressure can rise significantly above the state's 13.7 psi threshold in real-world conditions.

VAPOR PRESSURE OF CRUDE OIL

Pound per square inch (psi)



Note: Chart reflects vapor pressure readings of crude oil at different fill levels at 37.8°C/100°F.
Sources: Ametek; Reuters.

C. Chan, P. Rucker, 26/03/2015

REUTERS

Binary Mixtures

Air has profound effect on VPCR at low VL ratios

Air and methane have similar effect/curves

Gas Oil Ratio Determination

The ratio of the volume of gas to the volume of oil at standard conditions.

Primarily used in reservoir modeling or in production monitoring.

AITF developing miniaturized apparatus to determine CO_2, CO, H_2S, H_2, O_2 & N_2

Gas Oil Ratio Determination

Sample #	C1	
	HPLIS	GOR
1	0.007	0.005
2	0.000	0.006
3	0.017	0.016
4	0.005	0.004
5	0.012	0.010
6	0.004	0.005
7	0.012	0.008
8	0.014	0.007
9	0.039	0.025
10	0.023	0.022
11	0.006	0.005
12	0.011	0.007
13	0.014	0.010
14	0.006	0.006
15	0.024	0.023
16	0.033	0.045

HPLIS vs GOR
Methane
on 16 Various Crude samples

Thank you

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CCQTA, ASTM

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