

**UN/SCETDG/48/INF.62(Add.1)**

**UN/SCEGHS/30/INF.23(Add.1)**

---

**Committee of Experts on the Transport of Dangerous Goods  
and on the Globally Harmonized System of Classification  
and Labelling of Chemicals**

4 December 2015

**Sub-Committee of Experts on the Transport  
of Dangerous Goods**

**Forty-eighth session**

Geneva, 30 November – 9 December 2015

Item 3 of the provisional agenda

**Listing, classification and packing**

**Sub-Committee of Experts on the Globally  
Harmonized System of Classification and  
Labelling of Chemicals**

**Thirtieth session**

Geneva, 9 – 11 December 2015

Item 2 of the provisional agenda

**Joint work with the Sub-Committee of  
Experts on the Transport of Dangerous  
Goods (TDG Sub-Committee)**

**Crude oil – classification and transport issues**

**Annex B: AITF Report (Crude Oil Sampling and Analysis)**

**Transmitted by the expert from Canada**

# ANNEX B - AITF REPORT (EN)



---

August 10, 2015

Transport Canada  
9th floor, Tower C, Place de Ville, 330 Sparks Street  
Ottawa, Ontario, K1A 0N5

Telephone: (613) 990-1138

**Attention: Tagenine Alladin**

Dear Tagenine,

**Re: Crude Oil Sampling and Analysis Conducted by AITF.**

The attached report summarizes the Crude Oil Sampling and Analysis results as requested by, and outlined in, the Memorandum of Understanding.

The results contained herein relate to the samples tested to date at Alberta Innovates - Technology Futures. This report should only be reproduced in full and with permission of Alberta Innovates - Technology Futures.

If you have any questions, please do not hesitate to call me at (780) 450-5538.

Sincerely,

A handwritten signature in blue ink, appearing to read 'Amanda Prefontaine', with a long horizontal flourish extending to the right.

Amanda Prefontaine  
Researcher  
Fuels and Lubricants

## Final Report

### Crude Oil Sampling and Analysis

#### Prepared by

Amanda Prefontaine, B.Sc.  
Fuels & Lubricants Group  
Alberta Innovates Technology Futures  
250 Karl Clark Road, Edmonton, Alberta T6N 1E4  
Tel: 780-450-5538; Fax: 780-988-9053  
Email: [amanda.prefontaine@albertainnovates.ca](mailto:amanda.prefontaine@albertainnovates.ca)

*For*

Tagenine Alladin, M.Sc.  
Scientific Research Advisor  
Safety Research and Analysis  
Transport Dangerous Goods Directorate, Transport Canada  
9th floor, Tower C, Place de Ville, 330 Sparks Street  
Ottawa, Ontario, K1A 0N5  
Telephone: (613) 990-1138  
Fax: (613) 990-2917

*Date issued: August 10, 2015*

*FL Project Order Id: FL14\_1881-001 to FL14\_1881-311*

Disclaimer:

1. This Report was prepared as an account of work conducted at ALBERTA INNOVATES - TECHNOLOGY FUTURES ("AITF") on behalf of Transport Canada. All reasonable efforts were made to ensure that the work conforms to accepted scientific, engineering and environmental practices, but AITF makes no other representation and gives no other warranty with respect to the reliability, accuracy, validity or fitness of the information, analysis and conclusions contained in this Report. Any and all implied or statutory warranties of merchantability or fitness for any purpose are expressly excluded. Transport Canada acknowledges that any use or interpretation of the information, analysis or conclusions contained in this Report is at its own risk. Reference herein to any specified commercial product, process or service by trade-name, trademark, and manufacturer or otherwise does not constitute or imply an endorsement or recommendation by AITF.
2. Pursuant to the terms of the Memorandum of Understanding dated August 15, 2014, and in continuation of Transport Canada Work Order FL11\_1881, AITF confirms that Transport Canada is entitled to make such additional copies of this Report as Transport Canada may require, but all such copies shall be copies of the entire Report. Transport Canada shall not make copies of any extracts of this Report without the prior written consent of AITF. AITF further confirms that Transport Canada is entitled to distribute copies of this Report only to employees, agents and contractors of Transport Canada under terms that prohibit any further copying or distribution of the Report.
3. Any authorized copy of this Report distributed to a third party shall include an acknowledgement that the Report was prepared by AITF and shall give appropriate credit to AITF and the author/s of the Report.
4. Copyright AITF 2015. All rights reserved.

---

## LIST OF ABBREVIATIONS:

AITF	: Alberta Innovates –Technology Futures
FLG	: Fuels and Lubricants Group laboratories at AITF
LIMS	: Laboratory Information Management System
ASTM	: ASTM International
CAPP	: Canadian Association of Petroleum Producers
FPC	: Floating Piston Cylinder
TDG	: Transportation of Dangerous Goods
EOR	: Enhanced Oil Recovery
IBP	: Initial Boiling Point
FP	: Flashpoint
IR	: Infrared
GOR	: Gas/Oil Ratio
MSDS	: Material Safety Data Sheet
VLE	: Vapour Liquid Expansion
Bpd	: Barrels per day
SYNBIT	: Synthetic Bitumen
DILBIT	: Diluted Bitumen
PR-EOS	: Peng-Robinson Equation of State

---

## DEFINITIONS

**Battery Site:** A production unit where effluent from one or more wells is separated into its constituent phases (i.e., oil, gas and water) for metering and appropriate disposition.

**Condensate:** a complex combination of hydrocarbons in a liquid form, primarily separated and/or condensed from natural gas, and consisting of hydrocarbons mostly falling within, but not necessarily spanning, a carbon range of C2 to C30.

**Dead Crude Oil:** A term usually employed for crude oils that, when exposed to normal atmospheric pressure at room temperature, will not result in actual boiling of the sample.

**Dilbit:** Bitumen diluted with a natural gas condensate, refinery naphtha, or a mixture thereof. The percentage of diluent is approximately 20 to 30%.

**Fixed Gases:** Carbon dioxide, hydrogen sulphide, helium, hydrogen, oxygen and nitrogen.

**Free Water Knock Out:** A free-water knockout is designed to handle mostly water and sends the emulsion to the treater. When large amounts of water are produced, a free-water knockout, installed upstream of the treater, helps reduce the treater size requirements by disposing of all of the non-entrained water from the emulsion (free water), and greatly reduces fuel requirements for the treater.

**GOR:** Gas oil ratio - a measure of the volume of gas produced per volume of oil at standard conditions of temperature and pressure.

**Heavy Oil:** Crude oil with API gravity below 22.3°.

**Light Ends:** Low boiling components in a hydrocarbon liquid, present either naturally, or as a result of addition of a diluent. Light ends typically refer to components lower boiling (lighter) than n-decane, and frequently are restricted to n-pentane and lighter (Blackmore, 2014). Common light end components include C1 (methane), C2 (ethane), C3 (propane), iC4 (iso-butane), nC4 (n-butane), iC5 (iso-pentane), nC5 (n-pentane), C6 (hexane), C7 (heptane), C8 (octane) and C9 (nonane).

**Light Oil:** Crude oil with API gravity higher than 31.1°.

**Live Crude Oil:** Crude oil with sufficiently high vapour pressure that it would boil if exposed to normal atmospheric pressure at room temperature.

**Medium Oil:** Crude oil with API gravity between 22.3 and 31.1°.

**Produced Water:** Water naturally present in the reservoir or injected into the reservoir to enhance production, produced as a co-product when gas or oil is produced.

**Railbit:** Bitumen containing approximately 12 to 17% diluent.

**Sales Tank:** A tank where the treated oil is stored, ready to move on to the refinery or upgrader. It is often at this point that crude oil is sold by the producer to the refiner or other agent.

**Stabilized Crude Oil:** A crude oil having a Reid Vapour Pressure equivalent to or less than 82.7 kPa.

**Synthetic Bitumen:** Bitumen diluted with light sweet synthetic crude.

**Synthetic crude:** Produced by partially upgrading bitumen to produce a product similar to light sweet crude oil and is a blend of naphtha, distillate and gas oil range materials, with no residuum.

**Treater:** Separates oil, water and gas. A treater can accelerate separation by using heat, pressure, and sometimes chemicals and electrical mechanisms.

---

## ACKNOWLEDGEMENTS

This report was made possible thanks to the support and advice of many individuals, companies and organizations. I would like to extend my sincere thanks to all of them. Without their help, the completion of the project would not have been possible

I would like to thank the following people at Transport Canada for their guidance and support during the project: Tagenine Alladin, Barbara DiBacco and Patrick Juneau. My sincere appreciation also goes out to the Transport Canada Dangerous Goods inspectors in each sampling region and to the Alberta Transportation Dangerous Goods inspectors who accompanied the AITF sampling technologist on sampling trips.

I would like to express my appreciation to Dan Wispinski for his valuable technical support and constructive suggestions during the planning, development and completion of this project. His willingness to give his time so generously has been very much appreciated. I would also like to thank Jodi Johnston for her significant contribution to the preparation of the final report, her data analysis and organizational skills were invaluable.

My thanks and appreciations go to all of my colleagues in the Fuels and Lubricants laboratories at AITF. This large complex project would not have been successful without their commitment, effort and coordination. I would especially like to thank Pat Aberle and Matt McEachern for the hard work and long hours required to collect the samples, and Trevor Lockyer and Chris Goss for their expertise, commitment and technical support.

I would like to express my gratitude and thanks to the following people in industry for giving me such attention, time and co-operation:

Bill Lywood: Crude Quality Inc.  
Gordon Baux: Crescent Point  
David Russell and Brett Cameron: Gibsons Energy  
Randy Segato: Suncor  
Don Jordan: Cenovus Energy Inc.  
Chris Ryan: Tundra Energy Marketing Limited  
Dave Jordan: Tundra Oil and Gas  
Canadian Crude Quality Technical Association



## Table of Contents

LIST OF ABBREVIATIONS:	4
DEFINITIONS:	5
ACKNOWLEDGEMENTS:	7
1 Summary	15
2 Background	16
3 Objective	19
4 Sampling Plan: Regional Allocation of Samples	19
4.1 Selection of Sampling Locations	20
4.2 Sample Types	22
4.3 Sample List	23
5 Sampling Protocol	23
5.1 Environmental Conditions at Time of Sampling	23
5.2 Crude Oil	23
5.2.1 Pressurized Crude Oil Samples	24
5.2.2 Atmospheric Crude Oil Sample Collection	29
5.3 Produced Water	31
5.4 Sample Documentation	32
6 Testing Protocol	33
6.1 Crude Oil	33
6.2 Produced Water	34
7 Test Methods	34
7.1 Hydrogen Sulphide (H <sub>2</sub> S) Concentration	37
7.1.1 H <sub>2</sub> S in the Vapour Phase, ASTM D5705	37
7.1.2 H <sub>2</sub> S in Solution, APHA 4500 S2-E (produced water only)	37
7.2 ASTM D7678 Total Petroleum Hydrocarbons (produced water only)	38
7.3 pH (produced water only)	38
7.4 Flash Point, Closed-Cup Methods	38
7.4.1 ASTM D56 Tag Closed Cup	38
7.4.2 ASTM D93 Pensky-Martens Closed Cup	39

# ANNEX B - AITF REPORT (EN)



---

7.4.3 ASTM D3828 Small Scale Closed Cup .....	39
7.5 Initial Boiling Point, ASTM D86 .....	39
7.6 Water Content, ASTM D4007 .....	40
7.7 Density, ASTM D5002.....	40
7.8 Vapour Pressure .....	40
7.8.1 Vapour Pressure of Pressurized Samples at a V/L Ratio of 0.2:1 and 50°C, ASTM D6377 .....	40
7.8.2 Calculated Vapour Pressure of Pressurized Samples at a V/L Ratio of 0.02:1 and 50°C.....	41
7.8.3 Vapour Pressure of Atmospheric Samples at a V/L Ratio of 4:1 and 50°C, ASTM D323M.....	41
7.9 Gas-Oil Ratio (GOR) Determination and Gas Composition by GC .....	42
7.10 Compositional Analysis by Gas Chromatography .....	45
7.10.1 Light End Determination of Pressurized Samples (C1 to nC9), HPLIS-GC (ASTM D8003) .....	45
7.10.2 Light End Determination of Atmospheric Samples (C1 to nC9), ASTM D7900 .....	46
7.10.3 Boiling Point Distribution (nC4 to nC100), ASTM D7169 .....	46
7.10.4 Fixed GasC1 to C24 Composition and Boiling Point Distribution (C1 to nC100) of the Whole Crude Sample.....	47
7.11 Determination of Flammability of the Vapour Phase, ISO 10156.....	48
8 Results and Discussion: Crude Oil Samples.....	51
8.1 Density.....	51
53	
8.2 Hydrogen Sulphide in the Vapour Phase .....	55
8.3 Flash Point .....	60
8.4 Water Content .....	62
8.5 Boiling Point Distribution: Merging of HPLIS-GC/ASTM D7169 or ASTM D7900/ASTM D7169 Data.....	64
8.6 Initial Boiling Point.....	74
8.7 C1 to C24 Composition: Merging of ASTM D8003/ASTM D7169 or ASTM D7900/ASTM D7169 Data .....	80
8.1 Vapour Pressure at 50°C.....	122
8.1.1 Vapour Pressure at a V/L Ratio of 0.2:1 and 50°C, ASTM D6377 .....	122

---

---

8.1.2 Vapour Pressure at a V/L Ratio of 0.02:1 and 50°C, Calculated.....	128
8.1.3 Vapour Pressure at a V/L Ratio of 4:1 and 50°C, ASTM D323M.....	132
8.1.4 Calculated Vapour Pressure at a V/L Ratio of 4:1 and 50°C.....	137
8.1.5 Comparison of Vapour Pressures (50°C) at Each V/L Ratio.....	137
8.2 Gas Oil Ratio (GOR) and Flashed Gas GC Analysis.....	141
8.3 Assessment of Dangerous Goods Regulations .....	163
8.3.1 Toxic Inhalation Hazard .....	163
8.3.2 Flammable Liquids.....	164
8.3.3 Gases, Class 2.....	166
8.3.4 Flammable Gases, Class 2.1.....	166
9 Results and Discussion: Produced Water Samples .....	170
9.1 Hydrocarbon Content.....	170
9.1.1 Composition of the Hydrocarbon Layer.....	171
9.2 Flash Point.....	174
9.3 Hydrogen Sulphide in Produced Water.....	175
9.4 pH.....	178
10 Conclusions.....	179
10.1 Crude Oil.....	179
10.2 Produced Water.....	184
10.3 Summary.....	185
11 References .....	189

## LIST OF TABLES

Table 1: Major Oil Plays .....	20
Table 2: Regional Allocation of Samples .....	21
Table 3: Distribution of Sample Locations by Type of Facility .....	21
Table 4: Distribution of Crude Oil Samples by Type .....	22
Table 5: Sampling Locations and Sample Points .....	23
Table 6: Testing Protocol for Atmospheric Samples .....	33
Table 7: Testing Protocol for Pressurized Samples .....	33
Table 8: Testing Protocol for Produced Water .....	34
Table 9: Test Methods .....	35
Table 10: Difference in IBP – Average by Type .....	75
Table 11: Difference in IBP – Individual Samples .....	76
Table 12: Average, Minimum, Maximum Vapour Pressure (V/L 0.2:1, 50°C) and Standard Deviation – By Crude Oil Type .....	123
Table 13: Sum of Light Ends vs. Vapour Pressure .....	123
Table 14: Vapour Pressure at 50°C, V/L 0.02:1 (PR-EOS) and V/L 0.2:1 (ASTM D6377) .....	130
Table 15: Difference in Vapour Pressure (4:1) @ 50°, ASTM D6377 vs. ASTM D323M .....	135
Table 16: Fixed Gas and Light End Composition of Samples for which Vapour Pressure was measured at V/L 4:1 and 50°C by ASTM D6377 and ASTM D323M .....	136
Table 17: Vapour Pressure (4:1) @ 50°, ASTM D6377 vs. PR-EOS .....	137
Table 18: Vapour Pressure (50°), V/L 0.02:1, 0.2:1 and 4:1 .....	139
Table 19: Sum of Light Ends vs. GOR .....	143
Table 20: Packing Group Classifications of Class 3 Flammable Liquids .....	164
Table 21: Packing Group Classifications Based on Method of Determining IBP .....	165
Table 22: Hydrocarbon Content of Produced Water Samples .....	171
Table 23: Flash Point of Produced Water Samples .....	174
Table 24: Solution and Vapour Phase H <sub>2</sub> S Content of Produced Water Samples .....	176
Table 25: pH of Produced Water Samples .....	178



## LIST OF FIGURES

Figure 1: Proserv Type 5 10K Floating Piston Cylinder.....	25
Figure 2: Sampling Assembly.....	26
Figure 3: Pressurized Sample Collection at a Battery Site.....	28
Figure 4: Pressurized Sample Collection at a Truck Terminal.....	28
Figure 5: Atmospheric Sample Collection at a Gas Plant.....	30
Figure 6: Atmospheric Sample Collection at a Truck Terminal.....	30
Figure 7: GOR Apparatus.....	44
Figure 8: Average Density by Crude Oil Type.....	51
Figure 9: Distribution of Densities by Crude Oil Type.....	52
Figure 10: Average Density by Region.....	53
Figure 11: Distribution of Densities by Region.....	54
Figure 12: Average H <sub>2</sub> S in the Vapour Phase by Crude Oil Type.....	55
Figure 13: Distribution of H <sub>2</sub> S in the Vapour Phase by Crude Oil Type.....	56
Figure 14: Average H <sub>2</sub> S in the Vapour Phase by Region.....	57
Figure 15: Distribution of H <sub>2</sub> S in the Vapour Phase by Region.....	58
Figure 16: Average Flash Point by Crude Oil Type.....	60
Figure 17: Range of Flash Points by Crude Oil Type.....	61
Figure 18: Average Water Content by Crude Oil Type.....	62
Figure 19: Average Merged Boiling Point Distribution of All Oil Types.....	65
Figure 20: Average Merged Boiling Point Distribution of All Oil Types, 0% to 30% Off.....	66
Figure 21: Light Oil Merged Boiling Point Distributions.....	68
Figure 22: Medium Oil and Medium Diluted Oil Merged Boiling Point Distributions.....	69
Figure 23: Heavy Oil and Diluted Heavy Oil Merged Boiling Point Distributions.....	70
Figure 24: Bitumen and Diluted Bitumen (Dilbit) Merged Boiling Point Distributions.....	71
Figure 25: Synthetic Crude, Synthetic Bitumen (Synbit) and Diluted Synthetic Bitumen Merged Boiling Point Distribution.....	72
Figure 26: Condensate Merged Boiling Point Distributions.....	73
Figure 27: Average IBP by Crude Oil Type as Determined by GC and ASTM D86.....	75
Figure 28: ASTM D86 Distillation of a Dilbit, FL14_1881-007.....	79
Figure 29: Average C1 to C24 Composition of Light Oil, Medium Oil, Heavy Oil and Bitumen.....	82
Figure 30: Average C1 to C8 Composition of Light Oil, Medium Oil, Heavy Oil and Bitumen.....	83
Figure 31: Average C1 to C24 Composition of Condensate.....	84
Figure 32: Average C1 to C8 Composition of Condensate.....	85
Figure 33: Average C1 to C24 Composition of Heavy Oil, Diluted Heavy Oil, Bitumen and Diluted Bitumen.....	86
Figure 34: Average C1 to C8 Composition of Heavy Oil, Diluted Heavy Oil, Bitumen and Diluted Bitumen.....	87

# ANNEX B - AITF REPORT (EN)



---

Figure 35: Average C1 to C24 Composition of Bitumen, Synthetic Crude, Synthetic Bitumen, and Diluted Synthetic Bitumen.....	88
Figure 36: Average C1 to C8 Composition of Bitumen, Synthetic Crude, Synthetic Bitumen, and Diluted Synthetic Bitumen .....	89
Figure 37: Average C25+ Residue of All Crude Types.....	90
Figure 38: Light Oil C1 to C24 Composition.....	92
Figure 39: Light Oil C1 to C8 Composition .....	93
Figure 40: Medium Oil C1 to C24 Composition.....	94
Figure 41: Medium Oil C1 to C8 Composition.....	95
Figure 42: Condensate C1 to C24 Composition.....	96
Figure 43: Condensate C1 to C8 Composition .....	97
Figure 44: Heavy Oil C1 to C24 Composition.....	98
Figure 45: Heavy Oil C1 to C8 Composition.....	99
Figure 46: Diluted Heavy Oil C1 to C24 Composition .....	100
Figure 47: Diluted Heavy Oil C1 to C8 Composition .....	101
Figure 48: Synthetic Crude C1 to C24 Composition .....	102
Figure 49: Synthetic Crude C1 to C8 Composition.....	103
Figure 50: Dilbit C1 to C24 Composition.....	104
Figure 51: Dilbit C1 to C8 Composition.....	105
Figure 52: ASTM D8003 Chromatogram of a Synthetic Bitumen, FL14_1881-232 .....	107
Figure 53: ASTM D7169 Chromatogram of a Synthetic Bitumen, FL14_1881-232 .....	108
Figure 54: ASTM D7169 (C1 to C6) Chromatogram of a Synthetic Bitumen, FL14_1881-232; CS <sub>2</sub> not subtracted.....	109
Figure 55: ASTM D7169 (C1 to C6) Chromatogram of a Synthetic Bitumen, FL14_1881-232; CS <sub>2</sub> subtracted.....	109
Figure 56: ASTM D8003 Chromatogram of a Light Oil, FL14-1881-150 .....	110
Figure 57: ASTM D7169 Chromatogram of a Light Oil, FL14-1881-150 .....	111
Figure 58: ASTM D8003 Chromatogram of a Medium Oil, FL14_1881-154.....	112
Figure 59: ASTM D7169 Chromatogram of a Medium Oil, FL14_1881-154.....	113
Figure 60: ASTM D8003 Chromatogram of a Condensate, FL14_1881-073.....	114
Figure 61: ASTM D7169 Chromatogram of a Condensate, FL14_1881-073.....	115
Figure 62: ASTM D8003 Chromatogram of a Synthetic Crude, FL14_1881-220 .....	116
Figure 63: ASTM D7169 Chromatogram of a Synthetic Crude, FL14_1881-220 .....	117
Figure 64: ASTM D8003 Chromatogram of a Dilbit, FL14_1881-017.....	118
Figure 65: ASTM D7169 Chromatogram of a Dilbit, FL14_1881-017.....	119
Figure 66: ASTM D8003 Chromatogram of a Diluted Synthetic Bitumen, FL14_1881-021 ....	120
Figure 67: ASTM D7169 Chromatogram of a Diluted Synthetic Bitumen, FL14_1881-021 ....	121
Figure 68: Average Vapour Pressure (0.2:1) @ 50°C by Crude Oil Type .....	122
Figure 69: Vapour Pressure vs. Light End Hydrocarbons, Ordered by Vapour Pressure .....	124
Figure 70: Distribution of Vapour Pressure (0.2:1) @ 50°C by Crude Oil Type .....	125

---

# ANNEX B - AITF REPORT (EN)



---

Figure 71: Sample FL14_2881-244 Battery Configuration .....	127
Figure 72: Vapour Pressure @ 50°C, V/L 0.02:1 (PR-EOS) vs. V/L 0.2:1 (ASTM D6377)....	129
Figure 73: Average Vapour Pressure (4:1) @ 50°C by Crude Oil Type .....	132
Figure 74: Distribution of Vapour Pressure (4:1) @ 50°C by Crude Oil Type .....	133
Figure 75: Comparison of ASTM D6377 and ASTM D323M Vapour Pressures (4:1) @ 50°C	134
Figure 76: Measured and Calculated Vapour Pressures (50°C).....	138
Figure 77: Average GOR by Crude Oil Type.....	141
Figure 78: Distribution of GOR by Crude Oil Type.....	142
Figure 79: GOR vs. Light End Hydrocarbons, Ordered by GOR .....	144
Figure 80: Average Light Oil, Medium Oil and Condensate Flashed Gas Composition .....	145
Figure 81: Average Light Oil, Medium Oil and Condensate Fixed Gas Composition .....	146
Figure 82: Light Oil Flashed Gas Composition .....	147
Figure 83: Light Oil Fixed Gas Composition.....	148
Figure 84: Medium Oil Flashed Gas Composition.....	149
Figure 85: Medium Oil Fixed Gas Composition.....	150
Figure 86: Condensate Flashed Gas Composition .....	151
Figure 87: Condensate Fixed Gas Composition.....	152
Figure 88: Diluted Heavy Oil and Diluted Bitumen Flashed Gas Composition .....	153
Figure 89: Diluted Heavy Oil and Diluted Bitumen Fixed Gas Composition.....	154
Figure 90: Diluted Heavy Oil Flashed Gas Composition .....	155
Figure 91: Diluted Heavy Oil Fixed Gas Composition .....	156
Figure 92: Diluted Bitumen Flashed Gas Composition.....	157
Figure 93: Diluted Bitumen Fixed Gas Composition.....	158
Figure 94: Synthetic Crude, Synthetic Bitumen and Diluted Synthetic Bitumen Flashed Gas Composition .....	159
Figure 95: Synthetic Crude, Synthetic Bitumen and Diluted Synthetic Bitumen Fixed Gas Composition .....	160
Figure 96: Synthetic Crude Flashed Gas Composition.....	161
Figure 97: Synthetic Crude Fixed Gas Composition .....	162
Figure 98: Average Minimum % Flashed Gas in Air Required to Produce a Flammable Gas..	168
Figure 99: Minimum % Flashed Gas in Air Required to Produce a Flammable Gas – By Type .....	169
Figure 100: Produced Water Sample FL14_1881-084.....	172
Figure 101: ASTM D7169 Chromatogram of the FL14_1881-084 Hydrocarbon Layer .....	173
Figure 102: Produced Water H <sub>2</sub> S in Solution vs Vapour Phase.....	177

## 1 Summary

There is a critical requirement for the safe handling and transportation of crude oils, condensates and related petroleum products in order to ensure public safety. The appropriate handling protocols and transportation of dangerous goods classifications of these products are directly dependent on understanding the chemical and physical properties of these materials. Proper sampling practices and appropriate laboratory test methods are therefore critical to achieving this understanding. Misclassification of shipments of crude oils, condensates and related petroleum products can lead to the use of improper containers, insufficient safety plans and communication of inaccurate information to emergency responders.

Typically crude oils have been sampled into open containers which can result in the loss of light ends. The loss of light ends can impact the accuracy of subsequently measured properties of vapour pressure, flash point and initial boiling point – parameters used to assess TDG classifications. Erroneously low vapour pressure and high flash and initial boiling point can impact the TDG classification of a material resulting in an increased risk to public safety.

The properties of crude oils and condensates were determined utilizing sampling procedures designed to eliminate the loss of light ends by using a sealed pressurized system which maintains a single-phase sample. Samples obtained in this manner ensure that the resulting laboratory determinations are representative of the product.

Specialized and some newly industry developed laboratory procedures were used to qualitatively and quantitatively analyze crude oil samples in order to determine their physical and chemical properties. The new tools were designed to allow the direct interface of the sealed sample vessel to analytical instrumentation utilized in this study. The methods ensure samples are not compromised by fugitive evaporative losses before analysis. In some cases the results are compared to traditional analyses from samples collected in traditional sample containers. The analyses done were those that are required by TDG Regulations for classifications of Class 3 and to some extent Class 2. In addition to these tests, additional tests were performed on the crude oil to investigate and quantify the characteristics that are not currently assessed under TDG Regulations for classification as a Class 3.

This is the first comprehensive report of the properties of Canadian crude oils and condensates utilizing sealed sample containers and current modern laboratory methods. Samples were representative of all major types of product transported by rail and road. Bitumen, heavy oil, diluted heavy oil, dilbit, synbit, diluted synbit, light and medium oil, and condensates were



---

collected and analyzed. Production from British Columbia, Alberta, Saskatchewan, Manitoba, and North Dakota is represented.

In addition to the focus on crude oil, this project also looked at produced water. Produced water is transported via truck from a production site to a waste treatment facility or a water disposal well. As such a limited number of samples were obtained to evaluate properties impacting their safe transport.

Conclusions and observations in regards to sampling methodology, test method applicability and measured results are made in context of TDG regulations and classifications and beyond.

## 2 Background

As oil production in Canada has increased, the transportation of crude oil by rail and truck has also increased significantly over the past few years. Factors such as lack of pipeline capacity, the existence of extensive railroad networks, the length of time required to construct rail loading facilities vs. new pipelines, the flexibility of rail to deliver to multiple destinations, and the ability to ship undiluted bitumen in insulated and heated rail cars have all contributed to the increase.

Long distance transportation of crude oil to refineries is handled by two modes, pipeline and rail, primarily due to the ability to handle large volumes. In early 2013, monthly rail car loadings were at ~13,000 carloads, double what they were in the period between 2000 to 2010, and the Canadian Association of Petroleum Producers (CAPP) estimates that ~700,000 bpd of crude oil could potentially be transported to markets by rail in 2016 (CAPP, 2014). Transportation of crude oil by truck is not economical over long distances; however, they do play a role in carrying oil from production facilities to pipeline and rail loading facilities. If a battery does not have a connection to a pipeline or pipeline capacity is limited, trucks are used to transport the crude over relatively short distances. One midstream company, Gibsons Energy Inc., hauls ~250,000 barrels of energy products per day (Ricciotti, 2013). The magnitude of an incident involving a truck would potentially be less than one involving a train as the amount of product shipped by a truck is small compared to a unit train of rail cars and the frequency of incidents is low (Canadian Trucking Alliance, 2013). However, 70% of dangerous goods in Canada are transported by road and the most commonly transported dangerous goods are petroleum crude oil, gasoline and fuel oils. Trucks carrying dangerous goods use public roads and highways so attention needs to be paid to this mode of transportation as well.

With the increase in crude oil transportation and the several recent rail incidents including the tragedy in Lac- Mégantic where a unit train of petroleum crude oil derailed killing 47 people, there has been renewed focus on the classification of crude oil as a Class 3 flammable liquid and the role of light end components in classification. Volatility, flashpoint and flammability are important properties to consider for safe handling and transport of crude oil. These properties are directly related to the light ends concentration and composition.

As crude oil is a complex, multiphase mixture of many different components and its composition can vary widely depending on the source of the oil and location within the transportation chain, Transport Canada undertook a project for sampling and testing of crude oil from across different regions of Canada and at different points within the transportation chain in each region. The sampling and testing campaign provides Transport Canada with critical data that will increase their knowledge of the properties of Canadian crude oil.

The testing results will be used to assess the applicability of current classification requirements under Part 2 of the TDG regulations for Class 3 flammable liquids and Class 2.1 flammable gases, and to determine if there are any additional hazards posed by crude oil that are not currently being considered under these regulations. Flash point, initial boiling point and vapour pressure are the properties used to classify dangerous goods under Class 2 or 3. Other properties that will be used to characterize and assess the hazards of crude oil are the H<sub>2</sub>S content, C1 to C24 composition, boiling point distribution, gas/oil ratio and flashed gas composition.

Under Part 2 of the Transportation of Dangerous Goods (TDG) regulations, a flammable liquid is defined as a liquid that has a flashpoint less than or equal to 60°C (using a closed cup method) or is expected to be at a temperature greater than or equal to its flash point at any time while in transport. Flammable liquids are assigned to one of the following packing groups for the purpose of transportation based on thresholds for initial boiling point (IBP) and flashpoint (FP):

- a) Packing Group I: initial boiling point of 35°C or less at an absolute pressure of 101.3 kPa and any flash point;
- b) Packing Group II: initial boiling point greater than 35°C at an absolute pressure of 101.3 kPa and a flash point less than 23°C; or
- c) Packing Group III: if the criteria for inclusion in Packing Group I or II are not met.

A gas is defined under Part 1 of the TDG regulations as a substance that at 50°C has a vapour pressure greater than 300 kPa or that is completely gaseous at 20°C at an absolute pressure of 101.3 kPa and that is:

- 
- a) compressed (other than in solution) so that when it is packaged under pressure for transport it remains entirely gaseous at 20°C;
  - b) liquefied so that when it is packaged for transport it is partially liquid at 20°C;
  - c) refrigerated so that when it is packaged for transport it is made partially liquid because of its low temperature; or
  - d) in solution, so that when it is packaged for transport it is dissolved in a solvent.

The definition that could be applied to crude oil is (d); the gases that may be present are dissolved in the oil (the solvent).

Flammable gases, Class 2.1, are defined under Part 2 of the TDG regulations as gases that, at 20°C and an absolute pressure of 101.3 kPa:

- a) are ignitable when in a mixture of 13% or less by volume with air, or
- b) have a flammability range with air of at least 12 percentage points determined in accordance with tests or calculations in ISO 10156.

Produced water is water naturally present in the petroleum reservoir or injected into the reservoir to enhance production, and is produced as a co-product with the gas or oil. Components of produced water can include hydrocarbons, salts, metals, hydrogen sulphide (H<sub>2</sub>S), production chemicals and sediment. The composition varies based on the geochemistry of the producing formation, the type of hydrocarbon produced and the geographic location. The transportation and classification of produced water is of interest to Transport Canada. Production water is transported by truck from the production site to a waste treatment facility or a water disposal well. There have also been anecdotal reports of high concentrations of H<sub>2</sub>S present in some produced water shipments. For this reason, sampling and testing of produced water was also included in this project. As part of this project, the collected produced water samples were tested to determine the composition of the water and the hazards that may be present, in order to assess if the current TDG regulations are also applicable to produced water. Transport Canada has included ten produced water samples across different regions of Canada in the sampling campaign.

### 3 Objective

The objective of the project is to collect and characterize sixty-eight petroleum crude oil samples from across Canada destined for transport by rail and/or roadway. Ten produced water samples are also included in the sampling and testing objectives. The samples collected shall represent the range of crudes present in Canada in order to compile knowledge of the properties of Canadian crude oils and the various properties within a geographical region. The physical and chemical properties pertinent to the appropriate classification, subsidiary hazards, and packing group assignments, as per Part 2 of the TDG Regulations are assessed. Samples properties are also assessed for other hazards that may be present during transport.

### 4 Sampling Plan: Regional Allocation of Samples

In order to obtain a representative array of Canadian crude oil, allocation of samples across producing regions was based on the geographical production values and the modes of transportation used.

In 2013, total Canadian crude oil production was 3.5 million barrels per day (bpd). Production in eastern Canada was 230,000 bpd or 7% of total Canadian production. As the transportation of crude oil in eastern Canada is almost exclusively by ship and pipeline, samples from this region were not included in the sampling campaign.

In 2013, crude oil production in Western Canada was 3.2 million bpd. Of the total production, 1.3 million bpd was from conventional oil (including condensate). The balance of production, 1.9 million bpd, was from the oils sands. Most of the condensate comes from Alberta and British Columbia while most of the conventional production comes from Alberta and Saskatchewan, greater than 60% of which was light crude oil.

Alberta is the largest oil-producing province in Canada. In 2013, condensate production was at 123,000 bpd, conventional oil production was at 582,000 bpd and oil sands production totaled 1.9 million bpd. Saskatchewan is the second largest oil-producing province in Canada. The total (light and heavy) Saskatchewan oil production in 2013 was 486,000 bpd. Manitoba production in 2013 was 51,000 bpd. British Columbia accounts for 2% of conventional oil production and 14% of condensate production in western Canada (CAPP, 2014).

Crude oil produced in North Dakota, USA is also transported within Canada by rail and truck. As such, AITF recommended allocating a small number of the samples to crude oil from North

Dakota. Collecting the samples within the United States was not possible due to logistics and jurisdictional issues; as a result, these samples were collected at their destination in Canada.

#### 4.1 Selection of Sampling Locations

A number of industry and government sources as well as relevant industry, governmental and scientific publications were consulted in the selection of sampling sites. A preliminary list of sampling locations was generated based on the major oil plays in production in each province. Some of the major oil plays in each province are listed below in Table 1:

**Table 1: Major Oil Plays**

Region	Oil Producing Plays
<b>British Columbia (B.C.)</b>	Montney, Western Canadian Sedimentary Basin (WCSB)
<b>Alberta</b>	Cardium, Viking, Redwater, Duvernay, Montney, Pekisko, Alberta Bakken, Athabasca and Cold Lake oil sands
<b>Saskatchewan</b>	Bakken, Viking, Mannville, Frobisher, Midale
<b>Manitoba</b>	Viriden, Daly Sinclair, Waskada and Pierson
<b>North Dakota</b>	Bakken

Contact was made with producers in each region to gather information about the types of oil produced, status of the production sites, the inbound and outbound modes of transportation from the production/battery sites and the destination of the oil. In order to cover all aspects of crude oil transportation, contact was also made with truck, rail and transloading terminals to gather information about the types of oil transported, status of the sites and inbound and outbound modes of transportation.

The selection of specific sampling sites was based on the following criteria:

- Either the inbound or outbound mode of transportation was by truck or rail to ensure that the samples collected would be representative of crude oil in transport.
  - If a site was pipeline connected, a sample could still be collected if the oil was transported by truck or rail when pipeline capacity is limited.
- In each region, the samples were distributed among the major oil producing plays to ensure that the samples varied in composition and that a range of the different types of Canadian petroleum crude oil would be represented.

- Only samples of clean oil were collected, emulsions were not included in this sampling campaign.

The regional allocation and distribution of sample locations by type of facility are shown in Tables 2 and 3 respectively.

**Table 2: Regional Allocation of Samples**

Region	No. of Oil Samples	% of Total	No. of Produced Water Samples	% of Total
<b>British Columbia (B.C.)</b>	13	19	3	30
<b>Alberta (AB)</b>	33	49	4	40
<b>Saskatchewan (SK)</b>	13	19	1	10
<b>Manitoba (MB)</b>	7	10	2	20
<b>North Dakota Origin (N.D.)</b>	2	3	0	0

**Table 3: Distribution of Sample Locations by Type of Facility**

Sampling Location	No. of Samples	% of Total
<b>Battery</b>	29	43
<b>Gas Plant</b>	5	8
<b>Rail/Transloading Terminals</b>	23	33
<b>Truck Terminal</b>	11	16

#### 4.2 Sample Types

Classification of the samples according to sample type was based on the product information in the MSDS and information gathered from the sampling sites. The use of the terms sweet and sour refer to the total sulphur content and not the H<sub>2</sub>S concentration. Dilbit is defined as bitumen diluted with a natural gas condensate, refinery naphtha, or a mixture thereof. The percentage of diluent is usually approximately 20 to 30%. Synbit is defined as bitumen diluted with light sweet synthetic crude. Synthetic crude is defined as partially upgraded bitumen. It is similar to in composition to light sweet crude oil and is a blend of naphtha, distillate and gas oil range materials, with no residuum. The distribution of samples by type of crude oil is shown in Table 4.

**Table 4: Distribution of Crude Oil Samples by Type**

Sample Type		B.C.	AB	SK	MB	N.D. Origin	No. of Samples	% of Total Samples Collected
Condensate	Sweet	5	3			2	12	18
	Sour	2						
Light oil	Sweet	1	2	5	3		23	34
	Sour	5	4	2	1			
Medium oil	Sweet		4		3		14	21
	Sour			2				
	Sour, diluted		5					
Heavy oil	Sweet		3	2			9	13
	Sour			2				
	Sour, Diluted		1					
	Sweet, Diluted		1					
Bitumen, neat			1				1	1
Dilbit			5				5	7
Synbit			1				1	1.5
Synbit, diluted			1				1	1.5
Synthetic Crude			2				2	3
<b>Totals</b>		13	33	13	7	2	68	

## 4.3 Sample List

A detailed list of crude oil and produced water samples collected and analyzed at AITF is provided in Appendix A.

## 5 Sampling Protocol

### 5.1 Environmental Conditions at Time of Sampling

Sampling was conducted during the period December 4, 2014 to May 1, 2015. The ambient temperature at the time of sampling was below 0°C December through February, and within the range of -25°C to 10°C for the entire project. The samples collected would be considered winter samples. These samples represent the worst-case scenario in terms of potential hazard as there would be minimal light end loss and the samples may tend to have higher vapour pressures than samples collected in the summer months.

### 5.2 Crude Oil

Crude oil samples were collected at batteries, gas plants, rail terminals, transloading facilities and truck terminals at the point closest to the outbound transportation loading point in order to be representative of the product being transported. At each sample location, five samples were collected; one pressurized (550mL) and four (1L) atmospheric samples. The sample locations and corresponding sample points are shown in Table 5.

**Table 5: Sampling Locations and Sample Points**

Sampling Location	Sample Point
Battery	<ul style="list-style-type: none"> <li>Sales oil tank</li> </ul>
Gas Plant	<ul style="list-style-type: none"> <li>Shipping line to a pipeline</li> <li>During truck loading</li> </ul>
Rail Terminal	<ul style="list-style-type: none"> <li>Meter shack between source and rail car.</li> <li>Storage tank</li> </ul>
Transloading Facility	<ul style="list-style-type: none"> <li>Meter shack between truck and rail car</li> </ul>
Truck Terminal	<ul style="list-style-type: none"> <li>Storage tank</li> <li>During truck unloading</li> </ul>

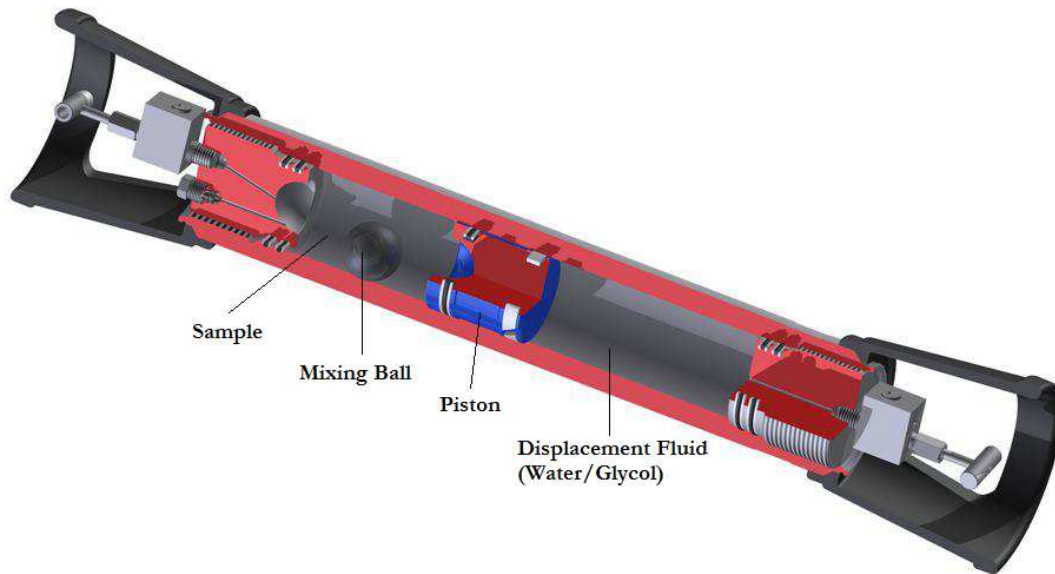


At both battery and gas plants, the crude transported represents a single source, either the product in the sales tank or the condensate produced at a gas plant. At rail terminals, transloading facilities and truck terminals, the crude transported can be either single source or a blend of multiple sources. Rail and truck terminals have above ground storage tanks with 20,000-barrel capacities that accumulate loads of crude oil as they come in. Samples collected from these tanks or as the product is loaded from the tank to a rail car would be representative of the blended product being shipped.

At transloading facilities, the crude oil is loaded from the truck onto the rail car through a meter shack. The rail cars can be filled with either a single product or a blend of products. The meter shack between the truck and rail car is the only available sample point, therefore if a blended product was transported; only the sources could be sampled. Basing the dangerous goods classification on source oil and not the blended product could lead to misclassification as the properties of the blended product may be significantly different from the source.

### 5.2.1 Pressurized Crude Oil Samples

In order to assess the impact of volatile components on the physical properties of the oils and their role in dangerous goods classification; pressurized samples were collected so that the loss of light ends would be minimized. The pressurized samples were collected in Proserv Type 5 10k, 700mL floating piston cylinders (FPC) shown in Figure 2. This type of cylinder was selected for its volume capacity and because it is approved for use and transport within, and across borders, in the USA and Canada under US Department of Transportation Special Permit SP-12116 and Transport Canada Equivalency Certificate SU9269. The minimum volume of sample required for testing was 150mL. The use of a 700mL cylinder ensured that there would be sufficient volume to complete all tests and that there would be additional volume available if required.



**Figure 1: Proserv Type 5 10K Floating Piston Cylinder**

Collection of pressurized samples was performed using guidelines in ASTM D3700: Standard Practice for Obtaining LPG Samples Using a Floating Piston Cylinder and the CCQTA Single Phase Sampling Procedure. There is a perception that floating piston cylinders are difficult or impossible to use for the collection of low-pressure samples, as they require a sample source with sufficient pressure to move the piston and allow filling of the cylinder. At a number of sampling locations where the sample was collected from a storage tank, the only pressure on the sample was the tank head pressure, which was insufficient to move the piston. To overcome this challenge, AITF sampling technologists built a sampling assembly that connected the cylinder to the sample source and enabled sampling of both high and low pressure samples. The sampling assembly is shown in Figure 2.



**Figure 2: Sampling Assembly**

Prior to sampling, the pre-charge side of the FPC is filled with a 2:1 water/glycol mixture as a displacement fluid and the dead volume on the sample side is evacuated. At the sampling location, the 3-way valve on the sampling assembly is connected to the sampling side of the FPC by means of self-closing quick connects. The common port on the 3-way valve is connected to the sample point by a sampling hose. The third port of the 3-way valve has a purge/bottle sample line connected to it. An outflow line is also connected to the evacuation port on the pre-charge side (or backside) of the FPC to aid in collection and measuring of the glycol/water. A 100mL Bimba cylinder is connected to the sample hose between two check valves with 1psi cracking pressure. If there is sufficient upstream pressure, the sample will flow freely to the 3-way

---

valve and FPC. If there is insufficient upstream pressure, the Bimba cylinder with check valves can be used as a pump to fill the FPC.

The sample line is purged by opening the valve on the sample point and turning the 3-way valve to the purge position. At least two volumes of the Bimba cylinder are purged through the sample line into a waste container. When purging the sample through the Bimba cylinder, the cylinder handle is depressed completely to remove any trapped air/vapour. The 3-way valve is then turned to the sample cylinder position to purge the quick connect fittings.

To begin collecting the cylinder sample, the quick connect on the 3-way valve is attached to the FPC. The cylinder sample-side valve is then opened. The valve on the pre-charge side of the cylinder is slowly opened. As sample fills the cylinder, the displacement fluid is collected into a graduated cylinder. The valve must be opened slowly and then used to control the fill rate as rapid filling of the cylinder may result in gas bubbles in the sample. The fill rate should be a maximum of 200mL/min. The cylinder can only be filled to 80% of the volume, so once the level of displacement fluid in the graduated cylinder reaches 550mL, the 3-way valve is closed. If there is insufficient upstream pressure to fill the cylinder, the Bimba 'pump' cylinder can be used. When discharging to the FPC, the Bimba cylinder should only be depressed 75%. This will prevent any air trapped in the Bimba cylinder from being injected into the FPC. The sample point valve and the cylinder sampling valve are then closed and the pressure in the sampling line is released through the purge line on the 3-way valve. By closing the 3-way valve, then the cylinder sampling valve, followed by closing the pre-charge valve last, any hydraulic pressure on the sample will be released without expanding the sample. Plugs are installed on the cylinder sample valve and the pre-charge valve to prevent leaks should one of the valves loosen during transport/storage. Sample collection into a FPC is shown below in Figures 3 and 4.



Figure 3: Pressurized Sample Collection at a Battery Site



Figure 4: Pressurized Sample Collection at a Truck Terminal

Prior to analysis, all sample cylinders were checked for opening pressure. The cylinders were then pressurized to 500psi at room temperature and mixed every 5-10 minutes for 1 hour by flipping end over end. Pressurization of the cylinders to 500psi was performed to ensure that the sample remains single phase and that the pressure is sufficient to obtain reliable injection into transfer lines or instruments, as per ASTM D3700. After mixing, the sample cylinders were placed in an oven at 50°C for a minimum of 12 hours, and then mixed for 5 minutes to ensure the sample was single phase and paraffin wax (if any) was reconstituted.

## 5.2.2 Atmospheric Crude Oil Sample Collection

Collection of atmospheric samples into 1L glass bottles was performed using guidelines in ASTM D4057: Standard Practice for Manual Sampling of Petroleum and Petroleum Products. The sample bottle line of the sampling assembly was placed in the bottom 1/4 of the collection bottle and the 3-way valve was turned to the purge/sample line position. The rate of fill was controlled to prevent excessive aeration of the sample. Sample collection into a 1L glass bottle is shown in Figures 5 and 6.

Heavy oils with a density greater than 960kg/m<sup>3</sup> were too viscous to be sampled into floating piston cylinders. In these cases, an atmospheric sample was instead collected into a 1L glass bottle. Light ends are present in viscous crude but they are expected to be in low amounts and not easily released because of reduced ease of diffusion among the dense molecules so the loss of light ends would be minimal. The high viscosity and atmospheric sampling of these samples meant that some tests in the testing protocol could not be performed (ASTM D6377, HPLIS-GC and GOR) and modifications were necessary for other tests (ASTM D323M).



Figure 5: Atmospheric Sample Collection at a Gas Plant



Figure 6: Atmospheric Sample Collection at a Truck Terminal

## 5.3 Produced Water

Produced water samples were collected at batteries and gas plants in British Columbia, Alberta and Saskatchewan from the storage tank at sites where a sample of crude oil was also collected. At a battery, the oil from the well is passed through a separator or treater where the liquid hydrocarbons, gas and water are separated. Gases are collected and routed for further processing. Hydrocarbons and produced water are routed to separate storage tanks. Since the produced water storage tank is at atmospheric conditions, some of the hydrocarbons present in the produced water may flash when the water is transferred to the storage tank. The hydrocarbons that did not flash remain in the liquid phase. It is the hydrocarbons in the liquid phase that pose a risk in the headspace of a tanker truck as the flashed hydrocarbons are already gone by the time the produced water is loaded onto a tanker truck. The hydrocarbons in the liquid phase may contribute to increased vapour phase hydrocarbon concentrations in the headspace of the tanker truck. Therefore, the collection of atmospheric samples was appropriate for this project. If analysis of the flashed gases were required, pressurized samples would have to be collected further upstream at the separator.

At each site, produced water samples were collected for hydrocarbon content, flashpoint, pH and H<sub>2</sub>S content testing. The type of sample bottle used, preservative added (if any) and the length of time between collection and testing was specified in each analysis method. One sample was collected into a 1L amber glass bottle for hydrocarbon content analysis. Sulphuric acid was added to prevent bacterial degradation of the hydrocarbons. One sample was collected in a 1L glass bottle for flash point and pH measurements. At seven of the ten sampling sites, one sample was collected into a 250mL plastic bottle for sulphide in water analysis. Sodium hydroxide was added to keep sulphide in the correct ionic form and zinc acetate was added to precipitate the sulphide out, keeping it stable for analysis. At seven of the ten sampling sites, two samples were collected into 1L bottles for measurement of H<sub>2</sub>S in the vapour phase. As the samples were collected under atmospheric conditions, there is a potential for loss of H<sub>2</sub>S during sampling. In fact, the test for H<sub>2</sub>S in the vapour phase must be done within 4 hours in order to obtain a valid reading.



---

## 5.4 Sample Documentation

The following information was recorded in the sampling logbook at every sampling site:

- Date
- Name of the company that owned the sampling site/facility
- Site/Facility Name
- Sample Name and Type
- Producer
- Originating source of the sample: formation/field/well
- Inbound and outbound modes of transportation
- Cylinder serial number
- Sample Point
- Temperature of the sample point (°C)
- Pressure at the sample point (psi)
- Volume of sample collected in the cylinder
- Elements upstream or downstream of the sample point, if applicable, such as
  - Treaters, separators, free water knock out, etc. and the conditions of each
  - Whether the sample is stored for weathering
  - Any processes the sample may undergo
- Material Safety Data Sheet (MSDS)
- Shipping Documents that would accompany a shipment of that sample.

Upon arrival at AITF, all samples were logged into the sample inventory system and assigned a sample ID (Laboratory Information Management System Number or LIMS #). Within the inventory system, each sample ID was linked to the sampling location and serial number of the cylinder used to collect the pressurized sample. A complete list of the sample IDs and the corresponding samples along with all documented sample information was sent to Transport Canada. The complete collected sample list is available as Appendix A.

## 6 Testing Protocol

### 6.1 Crude Oil

The atmospheric and pressurized samples were submitted to the Fuels and Lubricants laboratory at AITF for the tests in Tables 6 and 7 respectively.

**Table 6: Testing Protocol for Atmospheric Samples**

Test	No. of Samples Tested
<b>Flash Point</b> (ASTM D56, D93 or D3828)	68
<b>IBP</b> (ASTM D86)*	34
<b>VP @ 50°C</b> (ASTM D323M)*	44
<b>H<sub>2</sub>S in Vapour</b> (ASTM D5705)	68
<b>Water Content</b> (ASTM D4007)	68
<b>Density @ 15.6°C</b> (ASTM D5002)	68

\* The samples tested for IBP by ASTM D86 and VP by ASTM D323M were those that were shown to have the highest proportion of light ends (C1 -C4) in each of the regions, as determined by compositional data.

**Table 7: Testing Protocol for Pressurized Samples**

Test	No. of Samples Tested
<b>TVP @ 50°C and V/L 0.2</b> (ASTM D6377)	60*
<b>Gas/Oil Ratio (GOR) and Gas Analysis</b>	60*
<b>IBP and Composition</b> (HPLIS-GC/ASTM D7169)	60
<b>IBP and Composition</b> (ASTM D7900/D7169)	8
<b>Class 2.1</b> (ISO 10156)	60*

\*Some of the tests in Table 7 could not be performed on the heavy oil and bitumen samples due to atmospheric sampling and the viscosity of the samples. The samples were too viscous to be injected into the ASTM D6377 vapour pressure instrument and the HPLIS valve on the GC. Since the samples were already exposed to the atmosphere, a GOR could not be done. The vapour pressure of these samples was measured using ASTM D323M @ 50°C however; sample conditioning was done at ambient temperature to allow the sample to flow. Compositional analysis of the light ends was performed using ASTM D7900 rather than HPLIS-GC.

## 6.2 Produced Water

**Table 8: Testing Protocol for Produced Water**

Test	No. of Samples Tested
<b>Flash Point</b> (ASTM D56, D93 or D3828)	10
<b>Hydrocarbon Content</b> (ASTM D7678)	10
<b>Composition</b> (ASTM D7169)	1
<b>H<sub>2</sub>S in Vapour</b> (ASTM D5705)	7
<b>H<sub>2</sub>S in Solution</b> (APHA 4500)	7
<b>pH and conductivity</b>	10

Seven out of the ten samples were submitted for H<sub>2</sub>S in the vapour phase and seven were submitted for H<sub>2</sub>S in solution. Four of the ten produced water samples were submitted for both H<sub>2</sub>S analyses.

One produced water sample contained a hydrocarbon layer of sufficient volume to collect a sample for compositional analysis by ASTM D7169.

## 7 Test Methods

All test methods for crude oil and produced water are listed in Table 9 and described in the sections that follow.

# ANNEX B - AITF REPORT (EN)



**Table 9: Test Methods**

Test Method	Title
<b>APHA4500 S2-E</b>	Sulphur in Water, Extractable (Methylene Blue Auto-Colourimetry) Output: concentration of H <sub>2</sub> S in solution, mg/L Detection Limit: 0.002mg/L
<b>ASTM D56</b>	Standard Test Method for Flash Point by Tag Closed Cup Tester Output: flash point, °C Reproducibility: 4.3°C (Flash Point Below 60°), 5.8°C (At or above 60°C)
<b>ASTM D86</b>	Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, Initial Boiling Point Output: initial boiling point (IBP), °C Reproducibility: R=0.0595(Temp Evap. + 51.19), valid range 20 to 70°C
<b>ASTM D93</b>	Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester Output: flash point, °C Reproducibility: 10°C
<b>ASTM D323M</b>	Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), Modified. Output: vapour pressure at V/L 4:1 and 50°C, °C
<b>ASTM D3828</b>	Standard Test Methods for Flash Point by Small Scale Closed Cup Tester Output: flash point, °C
<b>ASTM D4007</b>	Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure) Output: water content, volume % Reproducibility: 0 to 0.3% (0.0% to 0.3% water), 0.28% (0.3% to 1.0% water)
<b>ASTM D5002</b>	Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer Output: density, kg/m <sup>3</sup> Reproducibility: 2.9 (density @ 700), 3.1 (density @ 750), 3.3 (density @ 800), 3.5 (density @ 850), 3.7 (density @ 900), 3.9 (density @ 950)
<b>ASTM D5705</b>	Measurement of Hydrogen Sulphide in the Vapor Phase Above Residual Oils Output: concentration of H <sub>2</sub> S in the vapour phase, ppm Reproducibility: (0.3*result)+15

# ANNEX B - AITF REPORT (EN)



Test Method	Title
<b>ASTM D6377</b>	Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR <sub>x</sub> (Expansion Method) Output: vapour pressure at V/L 0.2:1 and 50°C, kPa
<b>ASTM D7169</b>	Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography Output: boiling point distribution, mass %
<b>ASTM D7678</b>	Total Petroleum Hydrocarbons (TPH) in Water and Wastewater Solvent Extraction using Mid-IR Laser Spectroscopy Output: concentration of TPH in water, mg/L (ppm)
<b>ASTM D7900</b>	Standard Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography Output: light end composition, mass % Reproducibility: 0.1267(% m/m recovered +8)
<b>GOR/GC</b>	Atmospheric Flash of Hydrocarbon Samples for Gas-Oil Ratio Determination (GOR) Determination and Gas Composition by GC Output: GOR, m <sup>3</sup> /m <sup>3</sup> and flashed gas composition, mass %
<b>HPLIS-GC ASTM D8003</b>	Standard Test Method for Determination of Light Hydrocarbons and Hydrocarbon Boiling Point Distribution and Cut Point Intervals in Live Crude Oils and Condensates via Gas Chromatography Output: light end composition, mass %
<b>ISO 10156</b>	Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets Output: flammability range with air, % of gas in air

\*Reproducibility is not listed for some methods as it was not available or has not yet been determined for the material being tested for this project. For example, the reproducibility of ASTM D7678 is being determined by an inter-laboratory study and will be available sometime before 2016. The repeatability and reproducibility of ASTM D3828 have not been determined for temperatures below 20°C.

## 7.1 Hydrogen Sulphide (H<sub>2</sub>S) Concentration

### 7.1.1 H<sub>2</sub>S in the Vapour Phase, ASTM D5705

The concentration of hydrogen sulphide in the vapour phase of both the crude oil and produced water samples was determined by ASTM D5705 Standard Test Method for Measurement of Hydrogen Sulphide in the Vapour Phase Above Residual Fuel Oils. This method covers the field determination of H<sub>2</sub>S in the vapour phase (equilibrium head space) of a residual fuel oil. The method is applicable to liquids with a viscosity range of 5.5mm<sup>2</sup>/s at 40°C to 50 mm<sup>2</sup>/s at 100°C. The applicable range is from 5 to 4000 parts per million by volume. The test must be performed within 4 hours of sampling due to the volatile nature of H<sub>2</sub>S and the potential for loss of H<sub>2</sub>S during storage and handling.

A 1L glass test bottle is filled to 50% volume with sample from a filled container just prior to testing. In the test container, the vapour space above the sample is purged with nitrogen to displace air. The test container is then closed with a stopper fitted with a thermometer. The test container with sample is heated to 60°C for 30 minutes and then agitated on an orbital shaker at 220 rpm for 3 minutes. The stopper is removed and the bottle is sealed with aluminum foil. A length of stain detector tube is inserted through the foil and sample of the vapour phase is drawn through the tube.

The range of sample types collected required some modifications to the method. The test was performed at ambient temperature for most condensates. Volatile samples such as condensates will start to boil prior to reaching 60°C and a large portion of the sample will have been lost to evaporation once it reaches 60°C. For all other oil samples and produced water, the sample was placed in the water bath at 60°C. If the sample started to boil at any temperature below 60°C, it was immediately pulled out of the bath and tested. The test temperature of all samples was noted in the logbook.

### 7.1.2 H<sub>2</sub>S in Solution, APHA 4500 S2-E (produced water only)

The concentration of H<sub>2</sub>S in solution of the produced water samples was determined using APHA 4500 S2-E, Auto Colourimetry. This method covers the determination of sulphides in all types of aqueous samples in the range 0.002-0.200 mg/L with a detection limit of 0.002mg/L. The equivalent amount of H<sub>2</sub>S is then calculated by multiplying the concentration of sulphide by the ratio of the molar mass of H<sub>2</sub>S and sulphide. Sulphides present in solution are stabilized by the addition of zinc acetate (Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>) at the time of sample collection. Zinc Sulphide (ZnS) along with zinc hydroxide (Zn(OH)<sub>2</sub>) is precipitated by the addition of sodium hydroxide (NaOH). A mixed aliquot of sample containing ascorbic acid is pumped through a continuous

flow manifold where Sulphide is converted to a gas by the addition of hydrochloric acid (HCl) and then separated from the sample stream by a gas dialysis membrane and absorbed into a NaOH receiving stream. This stream is reacted with N,N-dimethyl-phenylenediamine and ferric chloride to produce methylene blue, an endpoint colour indicator, which is quantitated colourimetrically at 660 nm and compared with a series of standards. The samples were analyzed within seven days of sampling as per the method.

## 7.2 ASTM D7678 Total Petroleum Hydrocarbons (produced water only)

The definition of total petroleum hydrocarbons (TPH) depends on the analytical method used because TPH is the total concentration of the hydrocarbons extracted and measured by a particular method. The method used in this project to measure the hydrocarbon content of the produced water samples was ASTM D7678, Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy. This method covers the determination of total petroleum hydrocarbons (TPH) in water, and waste water, that are extractable from an acidified sample with a cyclic aliphatic hydrocarbon (cyclohexane), and measured by infrared (IR) absorption in the region of 1370 - 1380  $\text{cm}^{-1}$  (7.25 -7.30 microns). Polar substances and surfactants are removed by Florisil prior to IR measurement

One sample had a visible layer of hydrocarbon present. The heights of the hydrocarbon and water layers were measured and the amount of hydrocarbon was reported in ppm.

## 7.3 pH (produced water only)

The pH of each produced water sample was measured using a Mettler Toledo Seven Multi pH meter.

## 7.4 Flash Point, Closed-Cup Methods

The closed cup flash point of each sample was determined by ASTM D56, ASTM D93 or ASTM D3828. The method most appropriate to the sample type was selected based on viscosity and expected flash point.

### 7.4.1 ASTM D56 Tag Closed Cup

ASTM D56 Standard Test Method for Flash Point by Tag Closed Cup Tester covers the determination of flash point of liquids with a viscosity below 5.5  $\text{mm}^2/\text{s}$  at 40°C, or below 9.5  $\text{mm}^2/\text{s}$  at 25°C, and a flash point below 93°C. The sample is heated at a slow constant rate and an ignition source is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the ignition source causes the vapour above the sample to ignite. This method was used for one heavy oil sample.

## 7.4.2 ASTM D93 Pensky-Martens Closed Cup

ASTM D93 Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester, Procedure B covers the determination of the flash point of petroleum products in the temperature range from 40 to 370°C. The sample is heated and stirred at specified rates and an ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash is detected. This method was used for seven heavy oil samples and the undiluted bitumen sample.

ASTM D93, Procedure A was used for the produced water samples with slight changes to the method. The sample and sample cup were cooled to -7°C prior to testing. The sample was then mixed using a swirling rather than shaking motion to loosen any oil sticking to the sides of the bottle and distribute the oil throughout the water. Shaking the bottle would build up pressure and light ends would be lost when the lid was opened. While the liquid was still swirling, the sample was poured into the sample cup. The first ignition attempt was made once the sample reached 5°C. If the sample flashed at 5°C, the flash point would be reported as <5°C. Ignition attempts were continued every 1°C until the temperature reached the boiling point of the water.

## 7.4.3 ASTM D3828 Small Scale Closed Cup

ASTM D3828 Standard Test Methods for Flash Point by Small Scale Closed Cup Tester, Method B, covers procedures for flash point tests for petroleum products in the range of -30 to 300°C. Using method B, 2mL of sample is introduced into the test cup that is maintained at the expected flash point. After a specified time an ignition source is applied and a determination made whether or not a flash occurred. Then, the sample is removed from the test cup; the test cup and cover are cleaned, and the test temperature adjusted 5°C lower or higher depending on whether or not a flash occurred previously. A fresh sample is introduced and tested. This procedure is repeated until the flash point is established within 5°C. The procedure is then repeated at 1°C intervals until the flash point is determined to the nearest 1°C.

This method was used for all samples except heavy oils and bitumen, 60 out of the 68 samples collected. The lowest test temperature used was -30.0°C. If a sample flashed at -30°C, the flash point was reported as <-30°C

## 7.5 Initial Boiling Point, ASTM D86

The samples with the highest proportion of light ends in each region, as determined by compositional data, were submitted for initial boiling point determination by ASTM D86 Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure. This test method covers the atmospheric distillation of petroleum products using a laboratory batch



distillation unit to determine quantitatively the boiling range characteristics. The initial boiling point (IBP) is reported as the corrected temperature reading at the instant the first drop of condensate falls from the lower end of the condenser tube.

All samples were run using the Group 1 parameters and the results were reported as percent recovered. Group 1 requires the samples to be conditioned to below 10°C prior to analysis and it uses the slowest heating rate of all the groups in the method.

## 7.6 Water Content, ASTM D4007

The water content of each sample was determined by ASTM D4007 Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure). In this method equal volumes of crude oil and water-saturated toluene are placed into a cone-shaped centrifuge tube. After centrifugation, the volume of the higher density water and sediment layer at the bottom of the tube is read.

## 7.7 Density, ASTM D5002

The density at standard temperature (15.6°C) was determined using ASTM D5002 Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer. Approximately 1mL to 2mL of sample is injected into an oscillating tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. The density or relative density of crude oils is used for the conversion of measured volumes to volumes at the standard temperature of 15°C and for the conversion of crude mass measurements into volume units.

## 7.8 Vapour Pressure

Measurements of the vapour pressure were performed at 50°C in order to determine whether crude oils fit the definition of a gas as per Part 1 of the TDG regulations. As per the regulations, a gas is a substance that at 50°C has a vapour pressure >300 kPa.

### 7.8.1 Vapour Pressure of Pressurized Samples at a V/L Ratio of 0.2:1 and 50°C, ASTM D6377

The vapour pressure of the samples collected into floating piston cylinders was determined by ASTM D6377 Standard Test Method for Determination of Vapour Pressure of Crude Oil: VPCR<sub>x</sub> (Expansion Method) at a temperature of 50°C and a vapour/liquid (V/L) ratio of 0.2:1. ASTM D6377 allows for the introduction of sample directly from a pressurized cylinder into a temperature controlled measuring chamber with a moveable piston. Once the chamber is sealed, the volume is expanded by moving the piston until the final volume produces the specified V/L of 0.2:1. The temperature of the measuring chamber is then regulated to 50°C. Once

temperature and pressure equilibrium are reached, the measured pressure is recorded as the  $VPCR_{0.02:1}$  (50°C) of the sample.

## 7.8.2 Calculated Vapour Pressure of Pressurized Samples at a V/L Ratio of 0.02:1 and 50°C

The V/L ratio of 0.02:1 is significant in that it corresponds to the outage in rail cars which is approximately 5%. The vapour pressure at V/L 0.02:1 and 50°C was predicted using Aspen modeling software which utilizes the Peng-Robinson equation of state (EOS).

The first step was to use the software to predict the vapour pressure using a V/L ratio at which vapour pressure has already been measured, in this case, V/L 0.2:1. The V/L ratio was defined in the software as the volume of the vapour phase produced at 50°C to the volume of the liquid feed at room temperature. The measured density of the liquid feed and the predicted vapour volume using the equation of state was used in the calculation of the V/L ratio. The feed was then divided into components lighter than the C7 fraction and the C7+ fraction. The C7+ fraction is assumed to have a high boiling point. The measured vapour pressure data at V/L=0.2 was then fitted to that predicted by the Peng-Robinson EOS by adjusting the molecular weight of the C7+ fraction. Once the measured vapour pressure was fitted to the model, the vapour pressure at V/L 0.02:1 was calculated.

## 7.8.3 Vapour Pressure of Atmospheric Samples at a V/L Ratio of 4:1 and 50°C, ASTM D323M

The vapour pressure of the atmospheric samples was determined using ASTM D323 Standard Test Method for Vapour Pressure of Petroleum Products (Reid Method), Procedure A, modified for measurement at 50°C. ASTM D323 covers procedures for the determination of vapour pressure of gasoline, volatile crude oil and other volatile petroleum products at a V/L ratio of 4:1 and a temperature of 37.8°C. Procedure A is applicable to gasoline and other petroleum products with a vapour pressure of less than 180kPa. Since the requested measurement temperature was 50°C, the vapour pressure results cannot be referred to as Reid Vapour Pressure (RVP) as that term only applies to results obtained using a V/L of 4:1 and a temperature of 37.8°C. Therefore, in the body of the report the method is referred to as ASTM D323M and the results are presented as vapour pressure at V/L 4:1 and 50°C. The samples with the highest proportion of light ends in each region, as determined by compositional data, were submitted for vapour pressure by ASTM D323M at the requested temperature of 50°C.

At each sampling location, one 1L bottle was filled 70 to 80% volume for ASTM D323M testing. All samples submitted for D323M were conditioned at 0-1°C prior to testing along with the liquid chamber of the vapour pressure apparatus. The vapour chamber is stored in the 50°C

water bath prior to testing. The sample container is opened to the atmosphere and returned to the fridge for 2 minutes a total of three times for the purposes of air saturation of the sample. The liquid chamber is then filled to overflowing with the sample. The vapour chamber is immediately removed from the water bath and coupled to the liquid chamber. The apparatus is inverted to allow the entire sample in the liquid chamber to drain into the vapour chamber and then it is shaken vigorously eight times. The apparatus is turned right side up and immersed in the 50°C water bath. At intervals of 2 minutes, the pressure gauge is read and the shaking procedure is repeated. This procedure is repeated a minimum of five times until the last two consecutive gauge readings are the same. The pressure gauge is then removed from the apparatus immediately and compared to that of a pressure-measuring device. If there is a difference observed, the difference is added to the uncorrected vapour pressure when the pressure measuring device reading is higher or subtracted from the uncorrected vapour pressure when the pressure measuring device reading is lower, and the resulting value recorded as the vapour pressure of the sample at V/L 4:1 and 50°C.

ASTM D323M was also used for the heavy oils that were too viscous to be sampled into cylinders as they were also too viscous for the D6377 vapour pressure instrument. The conditioning temperature in the method was modified for these samples. A conditioning temperature of 20°C (ambient temperature) was used because the samples will not flow at 0°C and could not be transferred into the liquid chamber.

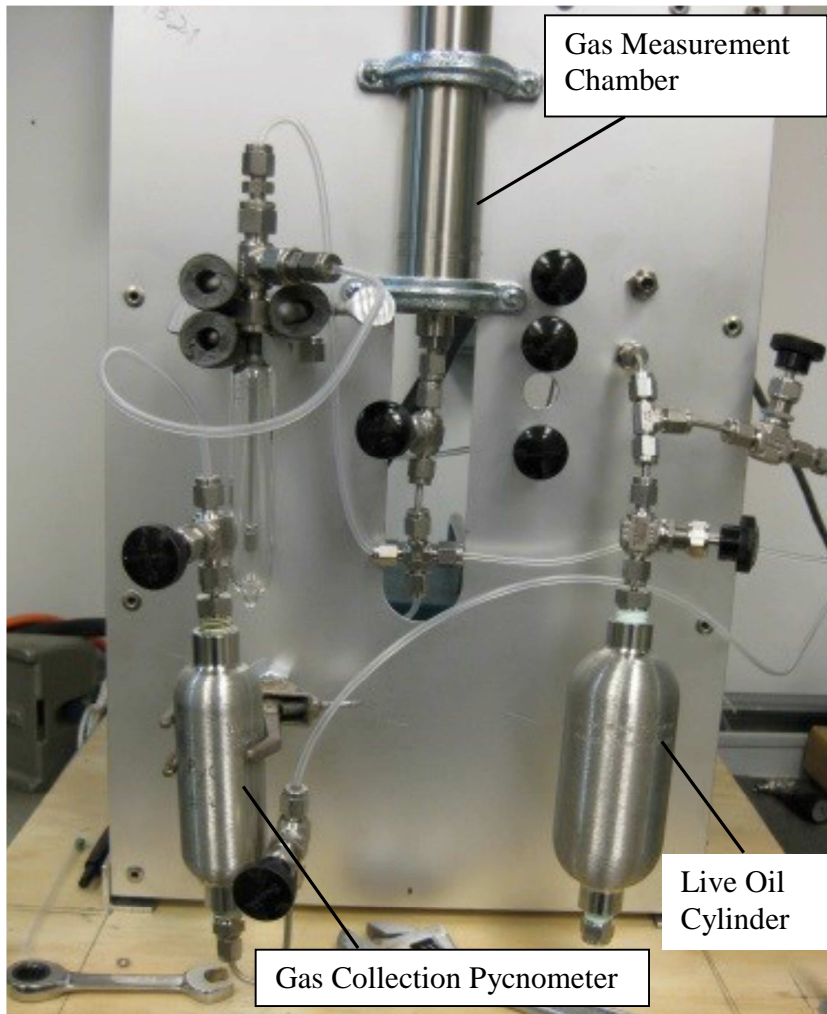
## 7.9 Gas-Oil Ratio (GOR) Determination and Gas Composition by GC

The gas oil ratio (GOR) is a measure of the volume of gas produced per volume of oil at defined conditions of temperature and pressure. The practice of measuring GOR is well known in industry and commonly utilized in reservoir modeling and field production monitoring. Reservoir samples can be obtained in excess of 69MPa, and normally contain highly saturated fixed gases. Similarly, large GORs are normally generated when measuring production rates from field separators. In these cases, use of commercially available equipment can be employed, due to their large vapour volume capacity.

Measuring the GOR in samples from pipeline and static holding sources, such as rail cars and storage tanks, is challenging due to the low volume of gas produced. The GOR process is gravimetrically based, and requires knowing either the mass or volume of produced gas, and being able to circulate the vapor through the flashed oil so gas-oil equilibrium is achieved at atmospheric pressure. As a result a low volume GOR flash apparatus was built to meet the requirements.

To perform the GOR analysis, a saturated oil sample is transferred isobarically into an evacuated, secondary pressure vessel (pycnometer) with a calibrated volume. The connection lines are evacuated to ensure that no light ends are lost and air contamination does not occur during the transfer. The mass of pycnometer before and after sampling is recorded and total volume of flashed oil and gas in the pycnometer post GOR analysis is calculated.

The sample pycnometer is then connected to the GOR apparatus via the collection trap and the circulation pump and the gas collection pycnometer are connected. The system is evacuated to 1mmHg to ensure there are no leaks. The sample pycnometer is opened to the system and allowed to stabilize. Using the circulation pump, the gas is circulated through the oil for one hour to ensure equilibrium. Atmospheric pressure is maintained during the circulation process by increasing the volume of the gas measurement chamber. When the pressure stabilizes during the circulation process, and the gas volume measurement chamber does not need adjustment, the flash is completed. The total evolved gas volume at atmospheric pressure is recorded. The GOR apparatus is shown in Figure 7.



**Figure 7: GOR Apparatus**

The liquid collection vessel and trap are weighed. The flashed oil is analyzed by gas chromatography and the oil density is measured. The GC results are validated against the results obtained using the ASTM D8003 method which has been calibrated using gravimetric standards. The oil density is used to convert the mass of oil remaining in the sample collection pycnometer to a volume at flash temperature. Since the total volume of the sample collection pycnometer is known, the remaining space is taken up by evolved gas and can be calculated by difference.

The gas is collected into an evacuated gas collection pycnometer. The composition of the flashed gas was determined by GC analysis and the gas molecular weight and density are calculated using the compositional results. This method covers the determination of C1 to C9

and CO<sub>2</sub>, H<sub>2</sub>S, He, H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>. The gas collection pycnometer is connected to the injection loop of the GC and the loop is then evacuated to prevent air contamination. Once evacuated, the loop is filled with gas from the pycnometer and the gas is injected into the GC. The GC has two detectors, a flame ionization detector (FID) which detects hydrocarbons C1 to C9+, and a thermal conductivity detector (TCD) which detects CO<sub>2</sub>, H<sub>2</sub>S, He, H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>. The GC was calibrated using certified reference gases. A three point calibration was performed for H<sub>2</sub>S and a single point calibration was performed for all other gases using a reference gas mixture. The concentration of nitrogen and oxygen in the samples is of interest to Transport Canada as they have an effect on the vapour pressure.

To ensure accuracy, several key components of the GOR apparatus require calibration; the atmospheric pressure gauge, the GOR temperature probe, gas pycnometer volume, the gas measurement chamber volume and the GOR dead volume. The atmospheric pressure gauge and the GOR temperature probe are sent to an approved vendor for calibration as per laboratory accreditation requirements. When returned, the pressure gauge is read directly and correction factors applied. The GOR temperature probe is set in baths with varying temperatures and the correction factor is determined. The sample collection pycnometer dead volume is determined gravimetrically by weighing the evacuated pycnometer then filling with pure water. Knowing the room temperature and density of water at that temperature the pycnometer volume is calculated. The gas volume measurement chamber is a high pressure stainless steel syringe with a cylindrical barrel. It is calibrated by measuring the cross sectional diameter of the barrel, near the top, middle and bottom using a traceable calibrated micrometer then calculating the cross sectional area and converting to cc/cm. The dead volume is determined by filling the evacuated GOR system with nitrogen to atmospheric pressure. A pycnometer is evacuated, weighed, filled with nitrogen and connected to the GOR. The mass loss is converted to a volume using the ideal gas law. By reduction of the system dead volume, and accurate volume calibrations, the GOR mass balance throughout the project yielded a bias of 30cc gas, which calculates to  $\pm 0.01 \text{ m}^3/\text{m}^3$ .

## 7.10 Compositional Analysis by Gas Chromatography

Hydrocarbon compositional analysis of the pressurized samples was done by a combination of two GC methods, either HPLIS-GC and ASTM D7169 or ASTM D7900 and ASTM D7169.

### 7.10.1 Light End Determination of Pressurized Samples (C1 to nC9), HPLIS-GC (ASTM D8003)

The HPLIS-GC method allows for the injection of pressurized samples into the GC, avoiding the loss of highly volatile components and maintaining sample integrity. This test method covers the determination of light hydrocarbons and cut point intervals by gas chromatography in live crude oils and condensates with VPCR4 up to 200 kPa at 37.8°C. Methane (C1) to hexane (nC6)

and benzene are speciated and quantitated. Samples containing up to 0.5 % mass methane, 2.0 % mass ethane, 5 % mass propane or 15 % mass isobutane may be analyzed. A 0.01 % mass lower limit exists for these compounds. This test method may be used for the determination of cut point carbon fraction intervals of live crude oils and condensates from initial boiling point (IBP) to 391°C (nC24). The nC24 plus fraction is reported. The results of this test method up to nC9 were combined with those from Test Method D7169 to give a full boiling point distribution of a crude oil.

This method uses a short, thick film non-polar column that has reasonable separation of C1 to nC5 components in a sample. After nC5 the separation is not as good, resulting in non-resolved peaks. This method uses known peak identifications up to nC5 and then cut point fractions from the rest of the sample. A cut point is defined as: the sample area from the end of one normal paraffin peak to the end of the next normal paraffin peak.. This area is converted into mass percent using an external standard that elutes 100% from the column. Generalized boiling point, density and molecular weight are used for the cut point fractions.

### **7.10.2 Light End Determination of Atmospheric Samples (C1 to nC9), ASTM D7900**

ASTM D7900 Standard Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography specifies a method to determine the boiling range distribution of hydrocarbons in stabilized crude oil up to and including n-nonane. A stabilized crude oil is defined as having a Reid Vapor Pressure equivalent to, or less than, 82.7kPa (V/L 4:1, 37.8°C). The results of this test method were combined with those from Test Method D7169 to give a full boiling point distribution of the crude oil. ASTM D7900 was used for the samples of heavy oil that could not be sampled into floating piston cylinders due to their viscosity, as they were also too viscous for the injection valve on the HPLIS-GC.

Samples were analyzed on a long (100m) non-polar chromatographic column with high separation ability. This column separates the hydrocarbons in order of their boiling points. A component table is used to determine the identity of peaks and their boiling points. For unknowns, a correlated retention time relative to known peaks is used to determine the boiling point. The material greater than nC9 is back flushed off the system, therefore an internal standard is used to determine the mass of eluted material.

### **7.10.3 Boiling Point Distribution (nC4 to nC100), ASTM D7169**

ASTM D7169 Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography covers the determination of the boiling point distribution and cut point intervals of dead crude oils and residues by using high temperature gas chromatography. The amount of residue (or sample

recovery) is determined using an external standard. The method extends the applicability of simulated distillation to samples that do not elute completely from the chromatographic system and is used to determine the boiling point distribution through a temperature of 720°C. This temperature corresponds to the elution of nC100.

Samples are analyzed on a non-polar chromatographic column that separates the hydrocarbons in order of their boiling points. These are correlated with the retention times, through a calibration curve obtained by running under the same conditions a known mixture of hydrocarbons, usually n-alkanes, covering the boiling range expected in the sample. Sliced peak intensities represent the sample amount distilled. Results are reported as a correlation between the boiling points and the percentages of the sample eluted from the column.

This test method uses a thin film capillary column, which results in the incomplete separation of C4 to C8 in the presence of large amounts of carbon disulphide, and thus yields an unreliable boiling point distribution corresponding to this elution interval. In addition, quenching of the detector during carbon disulphide elution results in unreliable quantitative analysis of the boiling distribution in the C4 to C8 region due to diminished response of the detector. The quality assurance sample used for this method is Athabasca bitumen that has a high residue. This bitumen covers the boiling range from C9 to C100 with a residue, the range of interest in this project.

#### **7.10.4 Fixed Gas and C1 to C24 Composition and Boiling Point Distribution (C1 to nC100) of the Whole Crude Sample**

The chemical composition of the sample from C1 to nC9 was determined from ASTM D8003 or ASTM D7900. A GOR flash was used to remove the fixed gases from the sample which were then analyzed by GC to give mass percentages of the fixed gases. ASTM D7169 data was used to determine the boiling point distribution of the sample from C9 to C100. The results of the three analyzes were then mathematically combined. Merging of the results eliminates the known bias in ASTM D7169 in the light boiling component composition due to the loss of light components during sample preparation, and quenching of the light boiling components by the carbon disulphide solvent (CS<sub>2</sub>). The results also give a more detailed look at the composition of the crude oil below nC5. The results of these three methods were used in two ways.

Boiling point distribution was determined in 1.0 mass percent intervals from IBP (0.5 mass % eluted) to nC100, with a residue above nC100 being determined. The same format as a traditional D7169 analysis is used, just with the bias removed.



The C1 to C24 compositional analysis was determined from the three methods as well. The compositional analysis includes the mass % of the fixed gases, and individual components up to nC5 and then cut point carbon fraction to C24. The cut point carbon fraction interval as used in this method is defined as the % mass obtained between the end of one n-paraffin peak to the end of the next n-paraffin peak, thus a temperature interval is not used to determine the cut points but rather the end points sequential of a n-paraffin peak pair. These fractions are given generalized boiling points, densities and molecular weights, as defined in ASTM D8003.

## 7.11 Determination of Flammability of the Vapour Phase, ISO 10156

In order to assess the applicability of a Class 2.1 Flammable Gas classification or subsidiary classification for crude oils, it must be determined whether the vapour phase of a crude oil sample is flammable.

Flammable gases, Class 2.1, are defined under Part 2 of the TDG regulations as gases that, at 20°C and an absolute pressure of 101.3kPa:

- are ignitable when in a mixture of 13% or less by volume with air, or
- have a flammability range with air of at least 12 percentage points determined in accordance with tests or calculations in ISO 10156.

The vapour phase above crude oil in a rail car or truck tank will contain gases that are in direct proportion to their relative volatilities and mole fractions in the liquid phase. It is the vapour phase that actually burns and the hazard presented by the vapour phase will depend on the amount of gas produced and its composition.

Since the GOR flashes were done at atmospheric pressure and ambient laboratory temperature (23°C), the evolved gas composition from the GOR analysis is what would be in the vapour phase above that sample of crude oil under atmospheric conditions and equivalent temperature. The calculation method described in ISO 10156, Gases and gas mixtures – Determination of fire potential and oxidizing ability for the section of cylinder valve outlets, was applied to the GOR flashed gas composition to determine if the vapour phase is a flammable gas. Calculations from Section 5 of ISO 10156, mixtures containing oxygen and flammables gases, were used.

The vapour phase of the crude oils contains flammable gases, nitrogen, other inert gases and oxygen. The other inert gases have different inerting equivalencies than nitrogen. The molar fractions of these inert gases are multiplied by their coefficient of equivalency and the relative volumes of equivalent nitrogen, flammable gas and oxidant are normalized to a total of 100%.

Equivalent Nitrogen:

$$F = \frac{100}{100 + \sum_{k=1}^p (K_k - 1)B_k}$$

where

F = Normalization Factor

$K_k$  = coefficient of equivalency of an inert gas relative to nitrogen

$B_k$  = molar fraction of the  $k^{\text{th}}$  inert gas in a gas mixture, in %

Flammable Gas Concentration:

$$\text{Flammable Gas Concentration} = F \times \sum_{i=1}^n A_i$$

where

$A_i$  = molar fraction of the  $i^{\text{th}}$  flammable gas in a gas mixture, in %

Oxidant Concentration:

$$OP = F \times x_o$$

where:

OP = oxidizing power

$x_o$  = molar fraction of oxygen, in %

A mixture containing flammable gases and oxidizing gases is flammable if it meets both of the following conditions:

- a) flammable gas concentration  $\geq L_m$
- b) flammable gas concentration  $> T_{ci,F}$

$$L_m = \frac{\sum A_i}{\sum \left(\frac{A}{L}\right)_i}$$

where

$L_m$  = lower flammability limit in air of a flammable gas mixture

$L_i$  = lower flammability limit in air of a flammable gas

---

$$T_{ci,F} = T_{c,m} \times \left(1 - \frac{OP}{21}\right), \quad T_{c,m} = \frac{\sum A_i}{\sum \left(\frac{A}{T_c}\right)_i}$$

where:

$T_{ci,F}$  = maximum content of flammable gas mixture and oxygen which, when mixed with nitrogen, is not flammable in air, in %

$T_{c,m}$  = maximum content of flammable gas mixture which, when mixed with nitrogen, is not flammable in air, in %

**8 Results and Discussion: Crude Oil Samples**

This section covers test results and analysis of 68 crude oil samples. It should be noted that where applicable, averages for sample types are presented in a figure. The values for diluted medium oil, bitumen, synthetic bitumen and diluted synthetic bitumen are single sample values only, not averages because only one sample of each these types was collected.

**8.1 Density**

The density of each crude oil sample was measured at 15.6°C using ASTM D5002. The average density and range of densities of each crude type and in each region are shown in Figures 8, 9, 10 and 11.

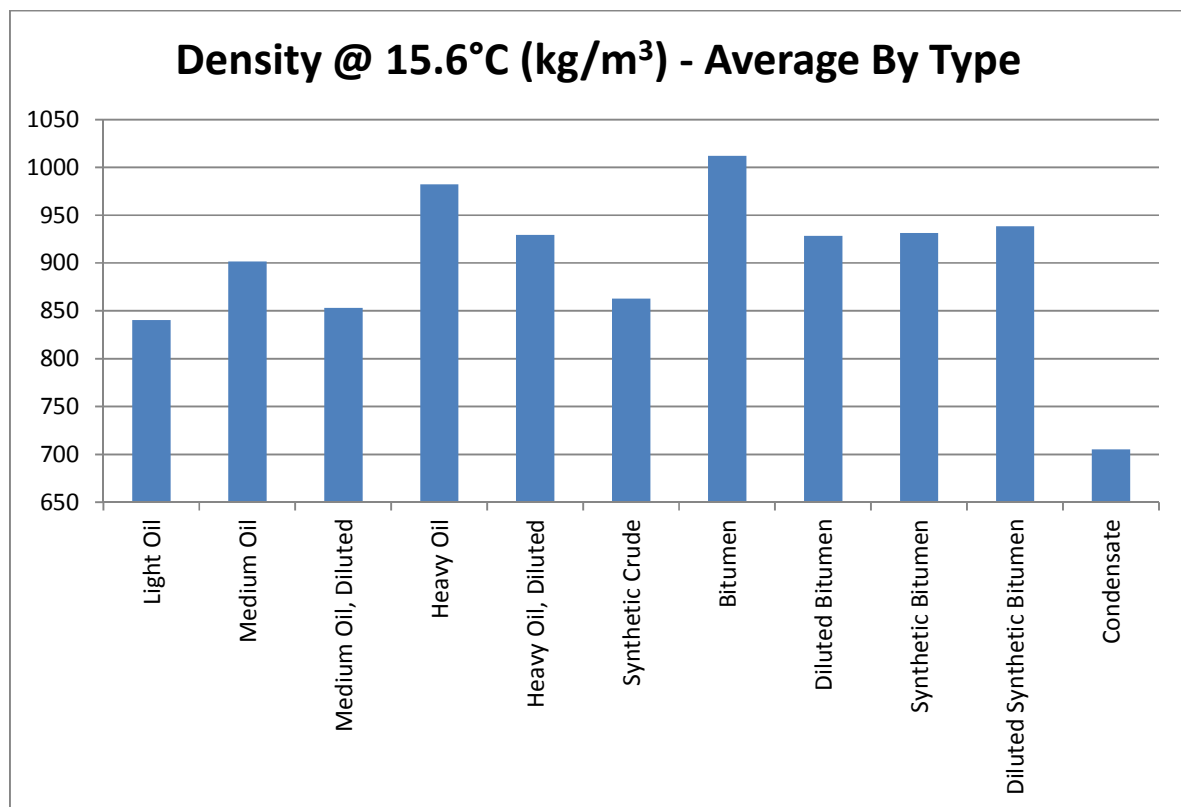
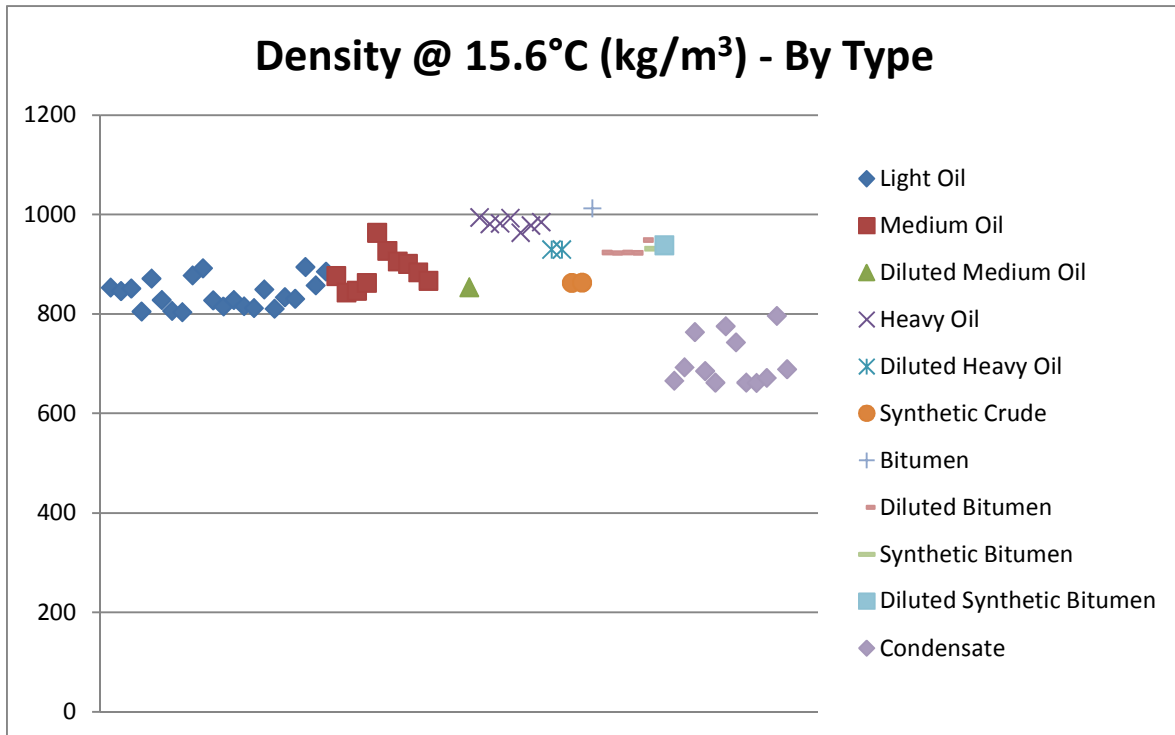


Figure 8: Average Density by Crude Oil Type



**Figure 9: Distribution of Densities by Crude Oil Type**

The average densities of the crude oils follow the pattern expected based on composition. Condensate, with the highest percentage of light ends and the least amount of C25+ residue has the lowest density. Bitumen, with the lowest percentage of light ends and the most C25+ residue has the highest density. All other samples fall in the range between condensate and bitumen according to their composition. The effect of diluent on the density is shown by the reduced density of the diluted samples of medium oil, heavy oil and bitumen as compared to the undiluted samples.

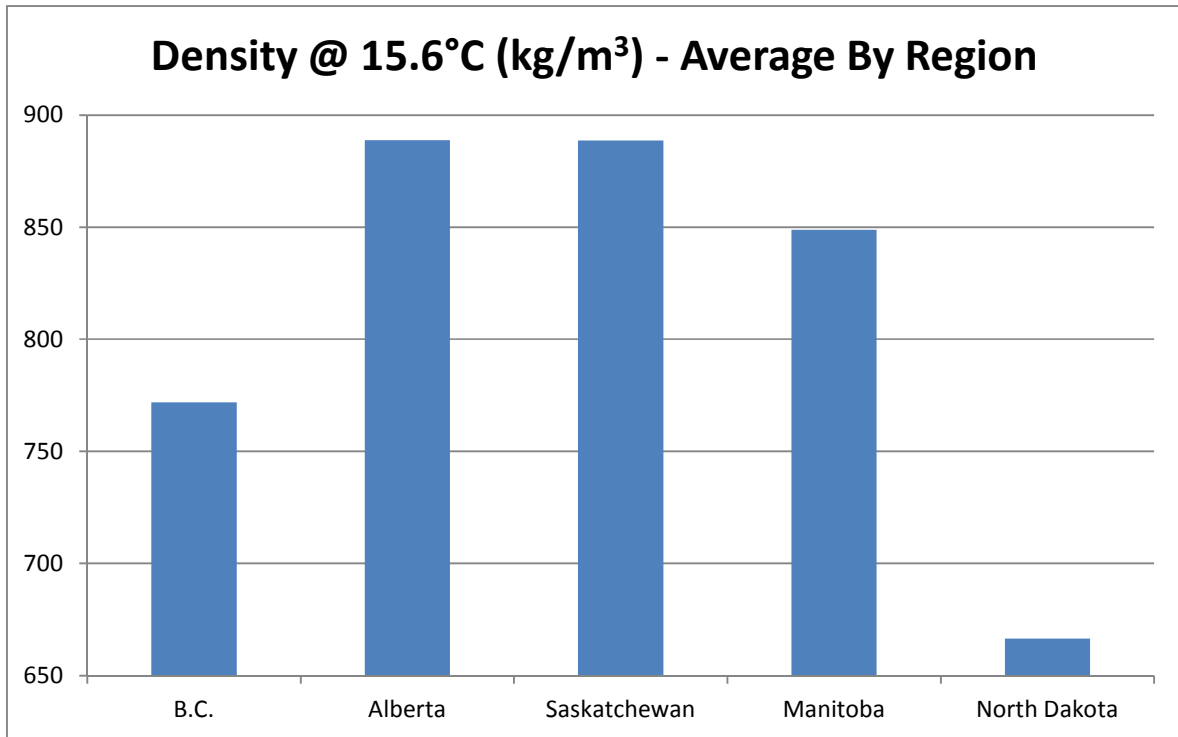


Figure 10: Average Density by Region

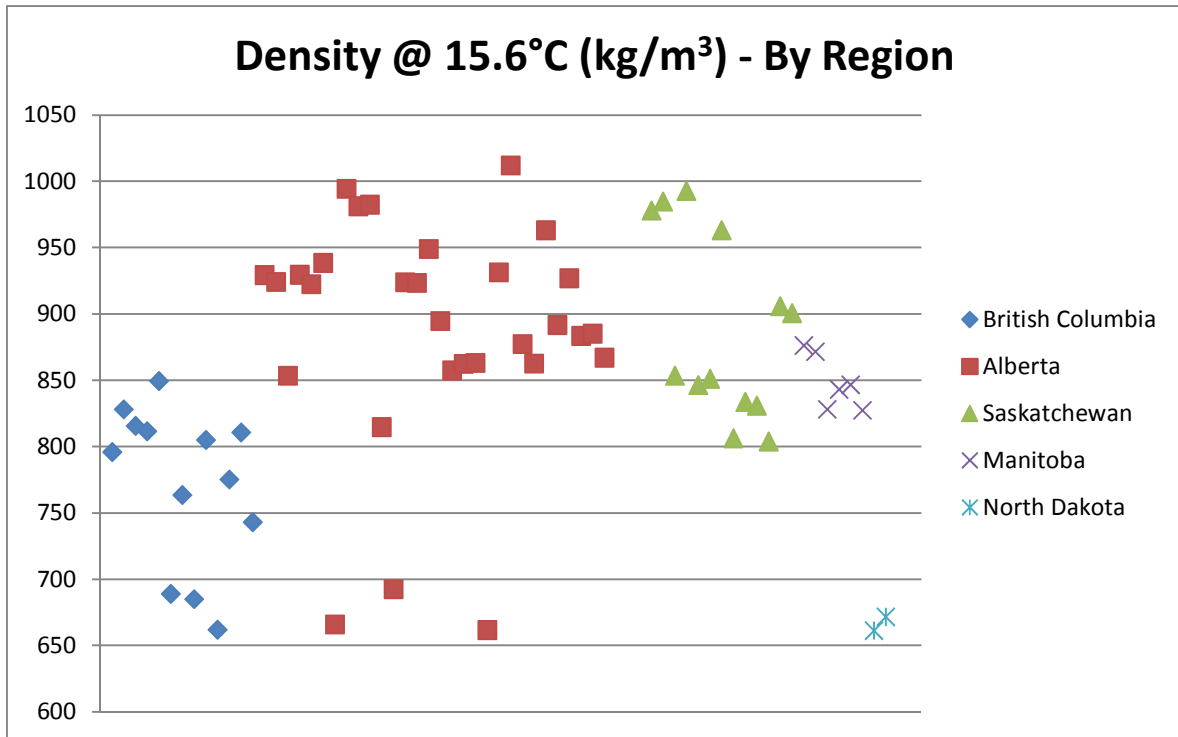


Figure 11: Distribution of Densities by Region

**8.2 Hydrogen Sulphide in the Vapour Phase**

The concentration of H<sub>2</sub>S in the vapour phase was measured by ASTM D5705. The average H<sub>2</sub>S concentration and range of concentrations of each crude type and in each region are shown in Figures 12, 13, 14 and 15.

It should be noted that the test temperature was modified depending on the crude oil type. The test was performed at ambient temperature for most condensates to prevent sample loss due to evaporation. For all other samples, the sample was placed in the water bath at 60°C. If the sample started to boil at any temperature below 60°C, it was immediately pulled out of the bath and tested. The test temperature of all samples was noted in the logbook.

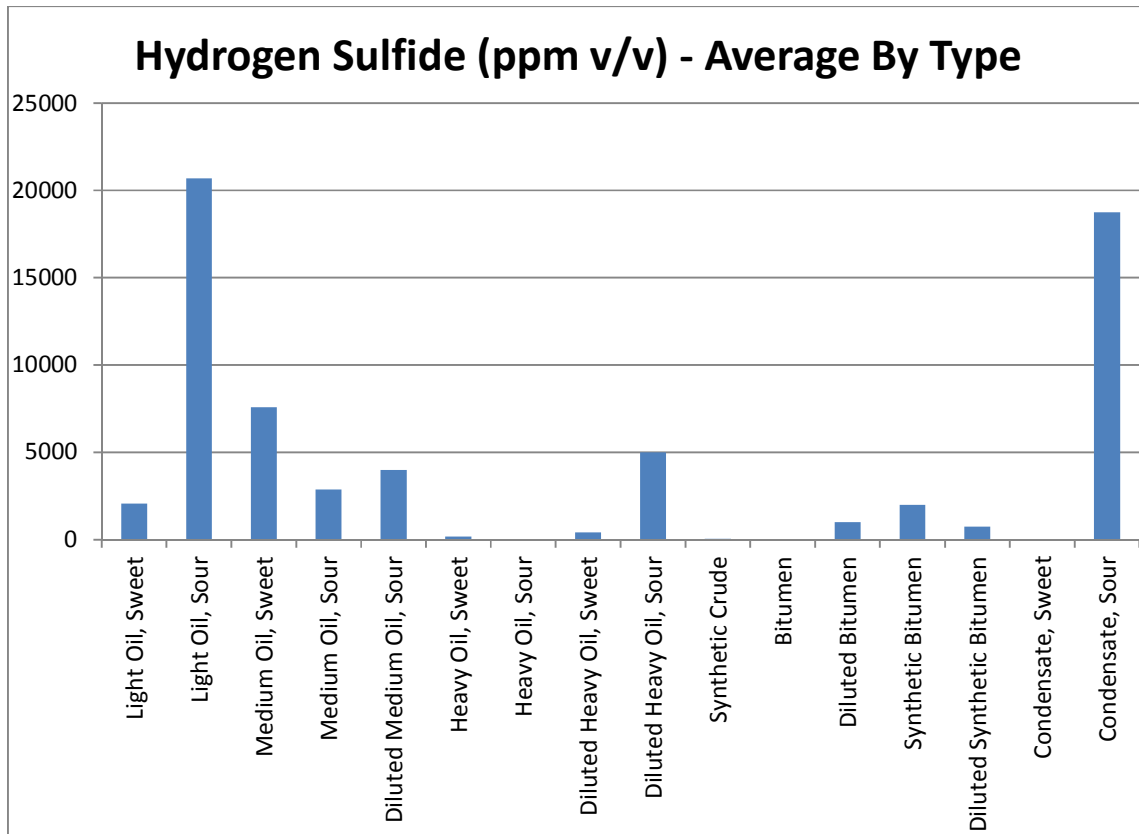


Figure 12: Average H<sub>2</sub>S in the Vapour Phase by Crude Oil Type



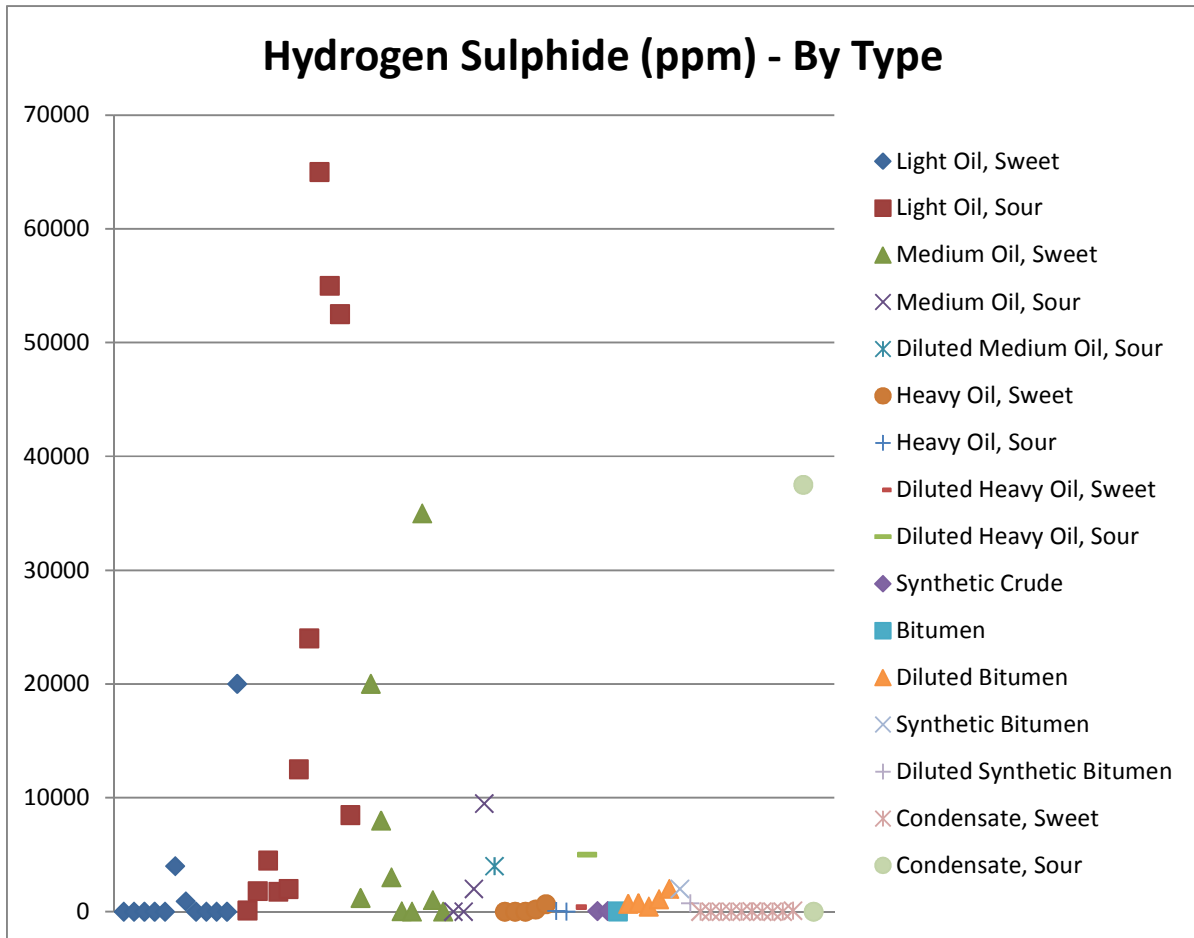


Figure 13: Distribution of H<sub>2</sub>S in the Vapour Phase by Crude Oil Type

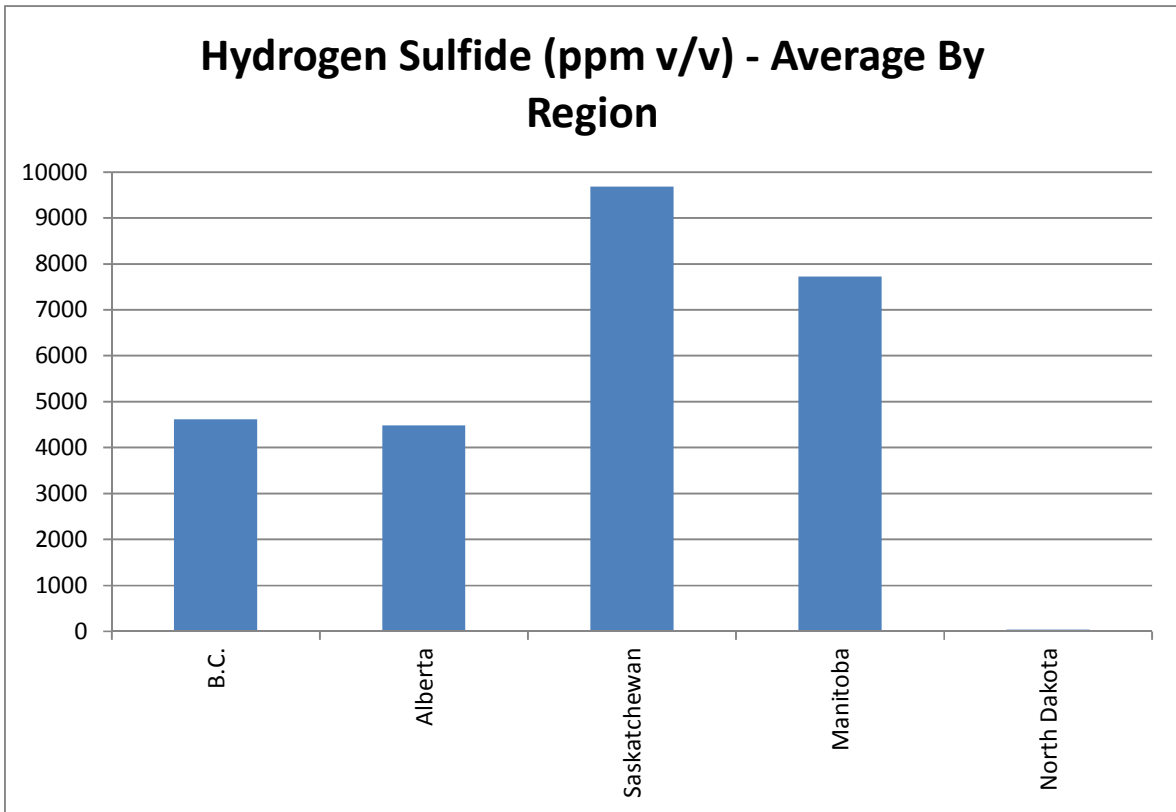


Figure 14: Average H<sub>2</sub>S in the Vapour Phase by Region

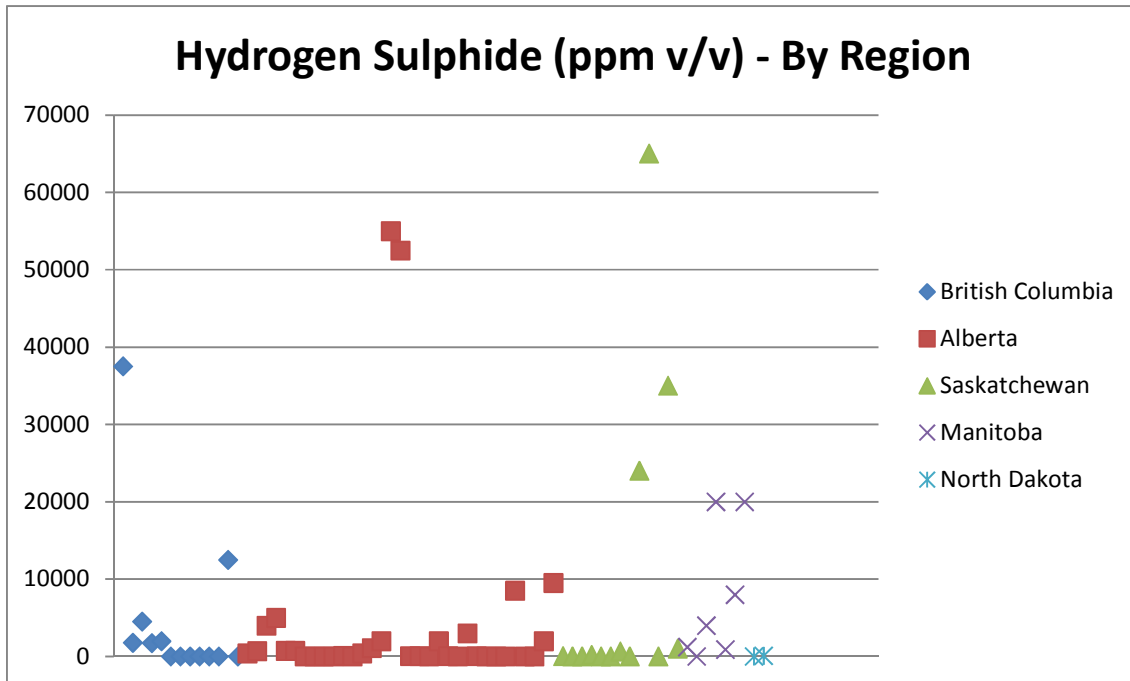


Figure 15: Distribution of H<sub>2</sub>S in the Vapour Phase by Region

It is a common misconception that the terms sweet and sour refer to the H<sub>2</sub>S content of oil. The terms in fact relate to the total sulphur content of a petroleum stream being less than 0.5 weight percent sulphur. While the use of “sweet” and “sour” in gas production is relatively accurate only because the bulk of the sulphur is in the form of H<sub>2</sub>S, the same cannot be said for liquid petroleum streams (Lywood & Murray, 2012). As can be seen in Figure 13, some sweet oils contain high concentrations of H<sub>2</sub>S in the vapour phase and some sour oils contain low concentrations of H<sub>2</sub>S in the vapour phase. Sample FL14\_1881-157 is a sweet medium oil yet the concentration of H<sub>2</sub>S in the vapour phase is 20,000ppm. Sample FL14\_1881-113 is a sour condensate yet the concentration of H<sub>2</sub>S in the vapour phase is 5ppm.

That being said, eight out of the nine samples with the highest concentrations (12,500ppm to 65,000ppm) of H<sub>2</sub>S in the vapour phase were sour samples. One was a condensate, six were light oils and one was a medium oil. The caveat when reading these high levels is that H<sub>2</sub>S concentration in the vapour phase varies as a function of headspace volume, temperature, agitation and the presence of scavengers therefore the value obtained by this test may not be representative of the concentration of H<sub>2</sub>S in the vapour space of a rail car or truck tank.

ASTM D5705 is commonly used as a field test method to determine the vapour phase H<sub>2</sub>S concentration of crude oil but there are a number of problems with this method. The most obvious issue is that the method is not designed for use with crude oils; the method scope states that it is for residual fuel oils. Residual fuel oils are what remain of crude oil after gasoline and distillate fuel oils have been extracted through distillation. As such, they do not contain light end components that will pressurize the sample container and cause the stopper to pop off as crude oils do.

Another issue with ASTM D5705 is that the procedure is not used consistently and many operators use a modified method. During the heating phase, pressure builds up within the test container and the stoppers can pop off. The fact that the stoppers pop off at all during heating is of concern since H<sub>2</sub>S will escape prior to measurement. To deal with this issue, operators may modify the method. Some operators clamp the stoppers down to prevent them from popping off, some leave the stoppers loose and others monitor the containers and push the stoppers back in if they pop off. Use of any of these modifications will have an effect on the quality of the results.

Another modification often made is to lower the temperature of the heating step. More volatile oils will start to boil prior to reaching 60°C and a large portion of the sample will have been lost to evaporation once it reaches 60°C. As the amount of H<sub>2</sub>S in the vapour phase is a function of temperature, the choice of bath temperature will affect the results.

ASTM D5705 is meant to provide an on-site assessment of H<sub>2</sub>S in the vapour phase for health and safety purposes. The test method cannot be used to simulate the concentration of H<sub>2</sub>S in storage or transport tank headspaces. The H<sub>2</sub>S concentration in the vapour phase varies as a function of headspace volume, temperature, agitation and the presence of scavengers. The method states that no general correlation can be established between this field test and actual vapour phase concentrations of H<sub>2</sub>S in storage or transport tanks. An example of the discrepancy between the field test and actual conditions was observed at a rail terminal. During loading of bitumen into the rail cars at 90°C, the operators' H<sub>2</sub>S monitors would alarm (monitor threshold=10ppm) and the procedure is to keep a safe distance during loading. The concentration of H<sub>2</sub>S in the vapour phase as determined by ASTM D5705 at 60°C was 40ppm. During loading of synthetic bitumen at ambient temperatures, the H<sub>2</sub>S monitors do not alarm however, the H<sub>2</sub>S concentration in the vapour phase as determined by ASTM D5705 at 60°C was 2000ppm.

ASTM D5705 does provide a measure of H<sub>2</sub>S present in the vapour phase and if the method was performed in a consistent manner using conditions of headspace and temperature encountered in transport, the results could be used as an indication of the level of risk.

### 8.3 Flash Point

The flash point of each sample was measured by the method appropriate to the sample; ASTM D3828, ASTM D56 or ASTM D93. The average flash point and range of flash points for each crude type are shown in Figures 16 and 17.

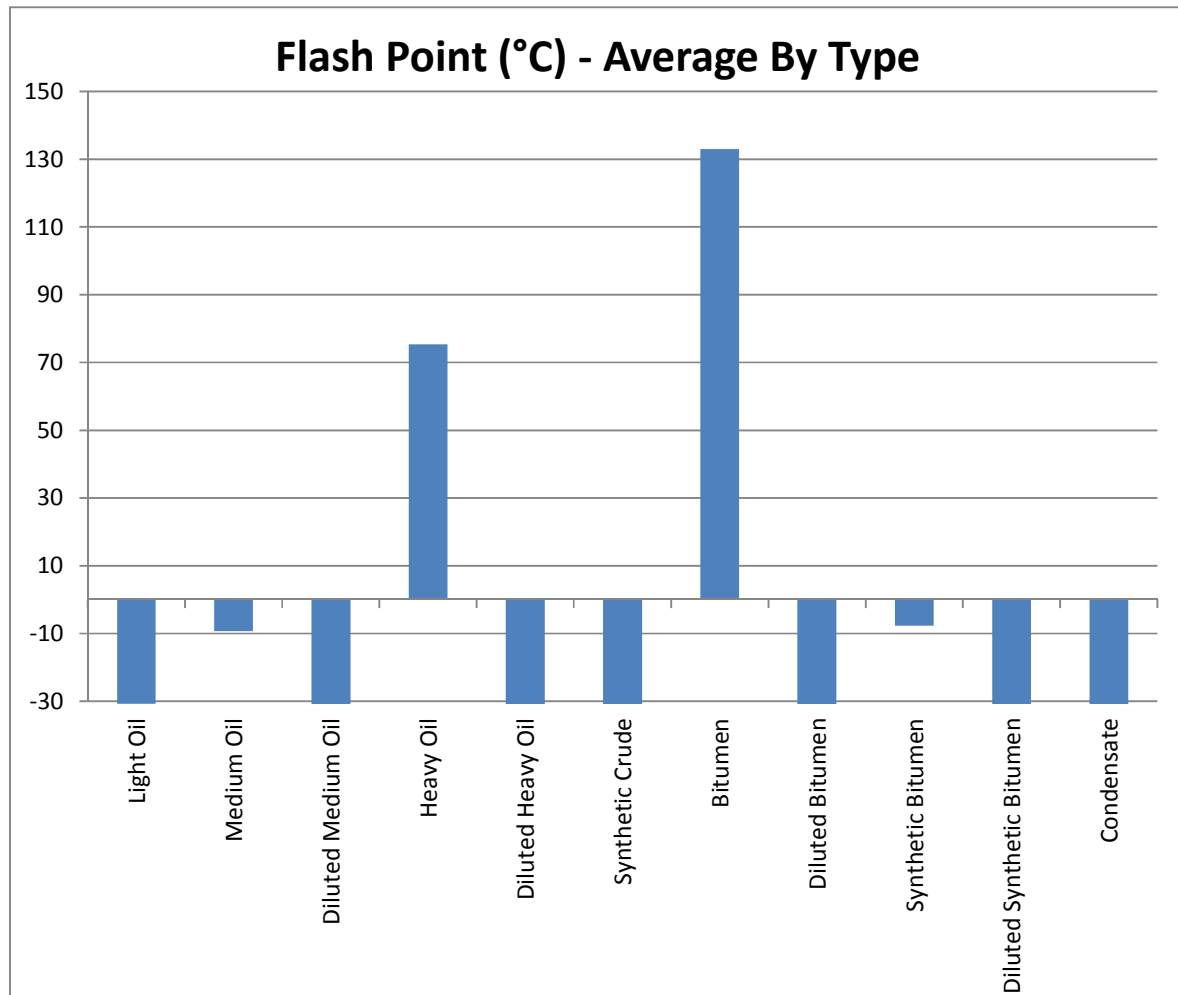


Figure 16: Average Flash Point by Crude Oil Type

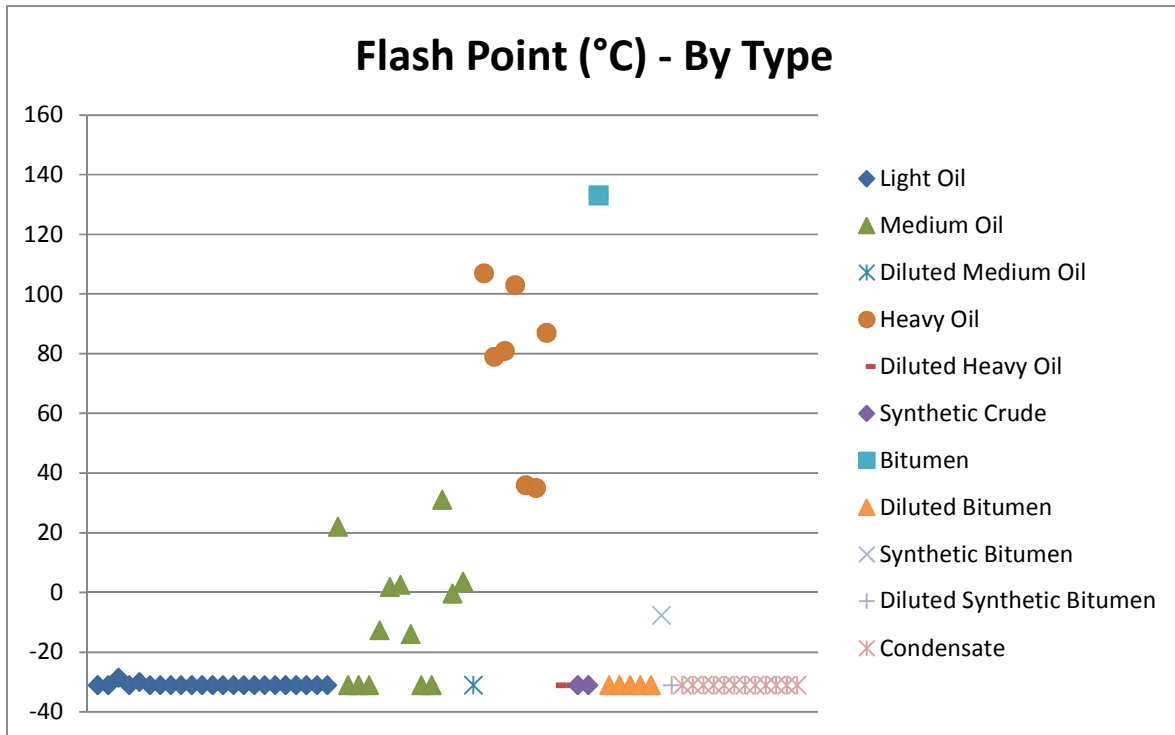


Figure 17: Range of Flash Points by Crude Oil Type

The flash point does not provide a means to differentiate between most oils; crude oils containing any appreciable amount of light ends will flash below 0°C. The theoretical flash point of pure butane is -60°C. Currently, equipment does not exist to measure the exact flash point. The lowest starting temperature that commercial flash point instruments can reach is -40.0°C.

However a difference was seen in diluted vs. undiluted samples. The light ends compositions of the diluted samples resulted in lower flash points than the undiluted samples. The flash point of all light oils, diluted oils, and condensates was <-30.0°C, except for two light oils which had flash points of -28.5°C and -30.0°C. There were six samples, five heavy oils and one bitumen, which had flash points above 60°C. These samples contained very little light ends. The percentage of C1 to C8 was less than 0.6%, which would account for the high flashpoints. As a result, these samples would not be classified as Class 3 flammable liquids under Part 2 of the TDG regulations.

All of these samples are have the potential to burn; however the flash point value provides no information regarding how long the product will burn, how hot the fire will be or if the light ends that ignite readily will provide enough energy to sustain combustion of the heavier ends.

**8.4 Water Content**

Recent work by API to model the vapour pressure of crude oil based on crude oil composition showed that water content is a contributing factor. The water content data collected in this project may be used towards future modelling work that Transport Canada plans to undertake in order to determine the vapor pressure of the crude oil samples. The water content of each sample was measured using ASTM D4007. The average water content and range of water contents for each crude type are shown in Figures 18 and 19.

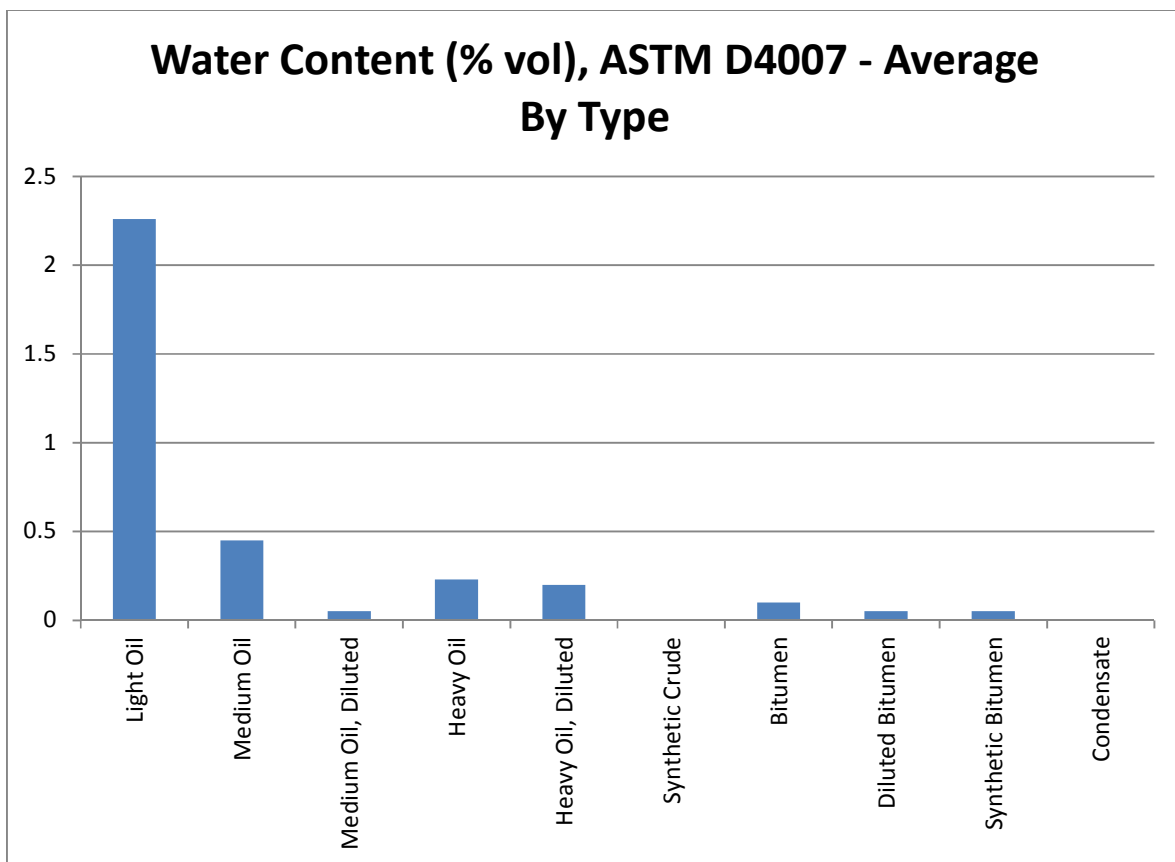


Figure 18: Average Water Content by Crude Oil Type

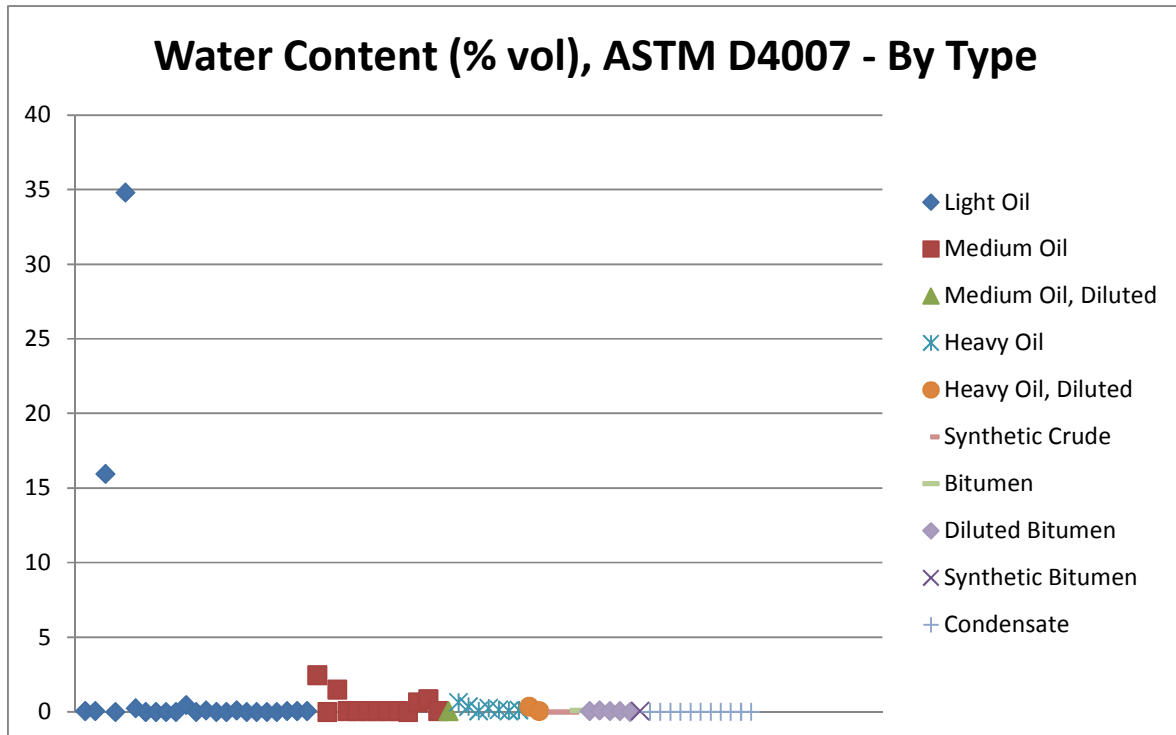


Figure 19: Distribution of Water Content by Crude Oil Type

As per the sampling plan, only clean samples of oil were to be collected, not emulsions. As a result, most samples had a water content of less than 0.5%. However, the information received regarding the battery components at the sampling sites was not always complete, and two samples collected were emulsions and had high concentrations of water. When first produced, oil can have high levels of impurities such as sand and water. As a result, crude oil emulsions are frequently shipped over short distances from a wellhead or a battery to another battery where it is cleaned and/or treated to break the emulsion. Virtually all of crude oil emulsion transportation is handled by trucks, with a small amount being transported by pipeline. FL14\_1881-068 and 148 had water contents of 15.95% and 34.8% respectively. Sample FL14\_1881-068 was sampled from a “truck-in” tank at a battery. Incoming trucks offload oil into the "truck-in" tank and the oil is pumped from this tank into a treater to remove the water. Once treated, the oil is transported by pipeline. In this case, the oil sampled was representative of what was transported to the site rather than from the site. Sample FL14\_1881-148 was sampled from a battery that did not have a free water knock out, which may account for the high water content.

ASTM D4007 measures the water in a sample which is removed by centrifugation. This method generally does not pick up emulsified or dissolved water (Crude Oil Quality Association, 2003).



The vapour pressure as measured by ASTM D6377 was performed on the samples in cylinders which were heated prior to testing. By heating the cylinders and keeping them upright, any free water would be at the bottom of the cylinder under the oil and thus would not have an effect on vapour pressure measurements. Transport Canada may want to consider determining the water content by Karl Fischer as well, which would determine the amount of dissolved, entrained and emulsified water. Heating of the cylinders would not remove this type of water so it may be possible to determine if it has an effect on the vapour pressure. Dissolved water will likely have small effect on the measured vapour pressure as the solubility of water in oil is very low. Emulsified water may have a greater effect on the measured vapour pressure as the amount of emulsified water would be greater than the amount of dissolved water.

### **8.5 Boiling Point Distribution: Merging of HPLIS-GC/ASTM D7169 or ASTM D7900/ASTM D7169 Data**

The complete boiling point distribution for each sample was determined by merging either the HPLIS-GC or ASTM D7900 data with the ASTM D7169 data. The HPLIS-GC/ASTM D7169 merge was used for sixty samples and the ASTM D7900/ASTM D7169 merge was used for eight samples (heavy oils and bitumen). The average boiling point distribution of all oil types is shown below in Figure 19. An expanded view of the average boiling point distribution between 0% to 30% of all oil types off is shown in Figure 20 to demonstrate the differences between the types of oil.

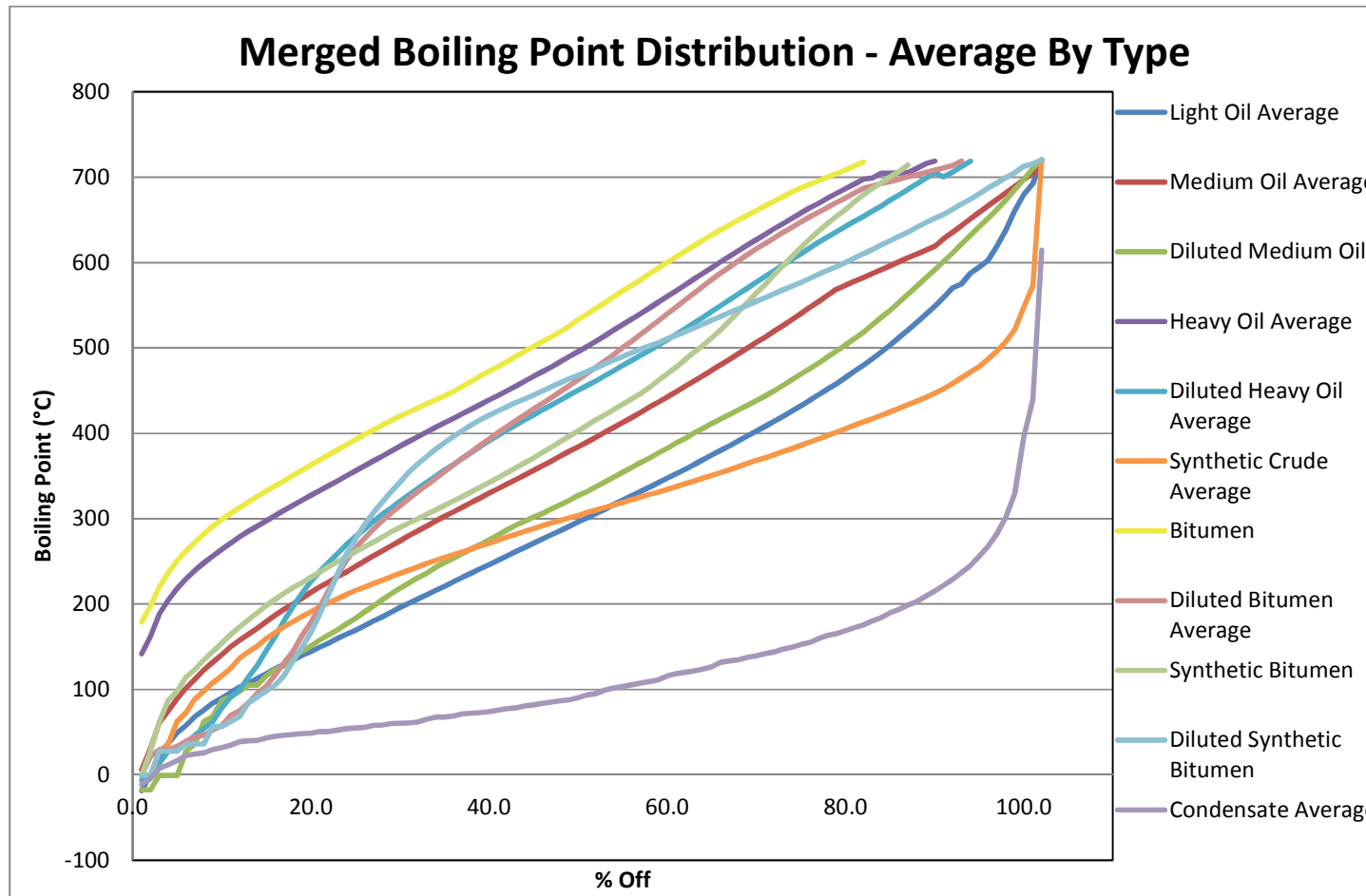


Figure 19: Average Merged Boiling Point Distribution of All Oil Types

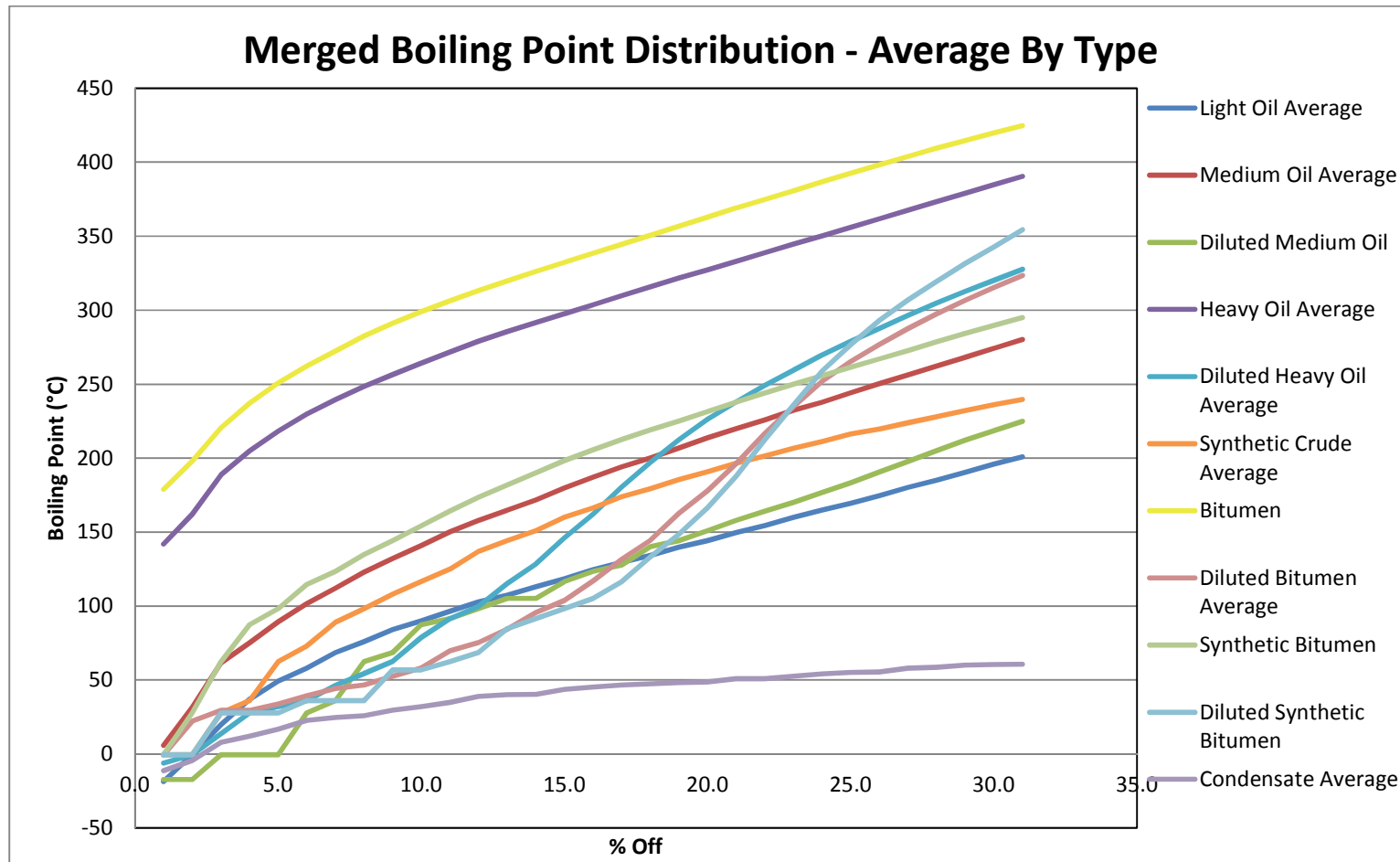


Figure 20: Average Merged Boiling Point Distribution of All Oil Types, 0% to 30% Off

As a benchmark for discussion, comparison of the graphs starts at 10% off. In Figures 19 and 20, the average condensate reaches 10% off by 40°C, 95% off by 300°C and does not have any residue. The light and medium oil averages show similar boiling point distributions to each other with approximately 10% of the sample off at 100°C, a steady rate of distillation after that, 95% off at 590°C and no residue. The light and medium oil curves are considered typical boiling point distribution curves. The average heavy oil and bitumen show similar boiling point distribution curves with the bitumen distilling at higher temperatures and having a higher percentage of residue. The heavy oil reaches 10% off at 242°C and has ~15% residue while the bitumen reaches 10% off at 300°C and has ~18% residue.

The average synthetic crude curve reaches ~10% off at 116°C, and a steady state of distillation is maintained until 500°C. At this point only 2% of the sample remains, which distills off by 720°C leaving no residue. This distillation curve corresponds to the composition of synthetic crudes, which are a blend of naphtha, distillate, and gas oil range materials, with no residuum.

The synbit curve shows the effect of the synthetic crude used to dilute the bitumen. The boiling point distribution follows the same trend as that of the synthetic crude up until 300°C when the temperature increases to distill the remainder of the sample due to the bitumen portion. The synbit also has ~13% residue compared to synthetic crude, which has 0%.

The effect of the diluent in the average diluted heavy oil, diluted synbit and dilbit curves is most clearly seen in the portion of the curve between 0-30% off (Figure 20). The remaining portion of the curve resembles the heavy oil, synbit and bitumen curves respectively. This correlates with the composition, which shows a bimodal distribution.

The possible implications concerning flammability are as follows. The initial boiling point of all the samples other than the heavy oil and bitumen is such that there is enough vapour present for the samples to ignite readily. The difference will be in how long they burn. Condensates will ignite and burn off quickly. The light and medium oils will ignite and burn as well but for longer and at higher temperatures. The dilbits, synbit and synthetic crudes contain sufficient light ends to ignite but it is not known if the ignition of the light ends will provide enough energy to sustain combustion of the heavier ends.

The individual boiling point distributions along with the average for each type are shown in Figures 21 to 26 below.

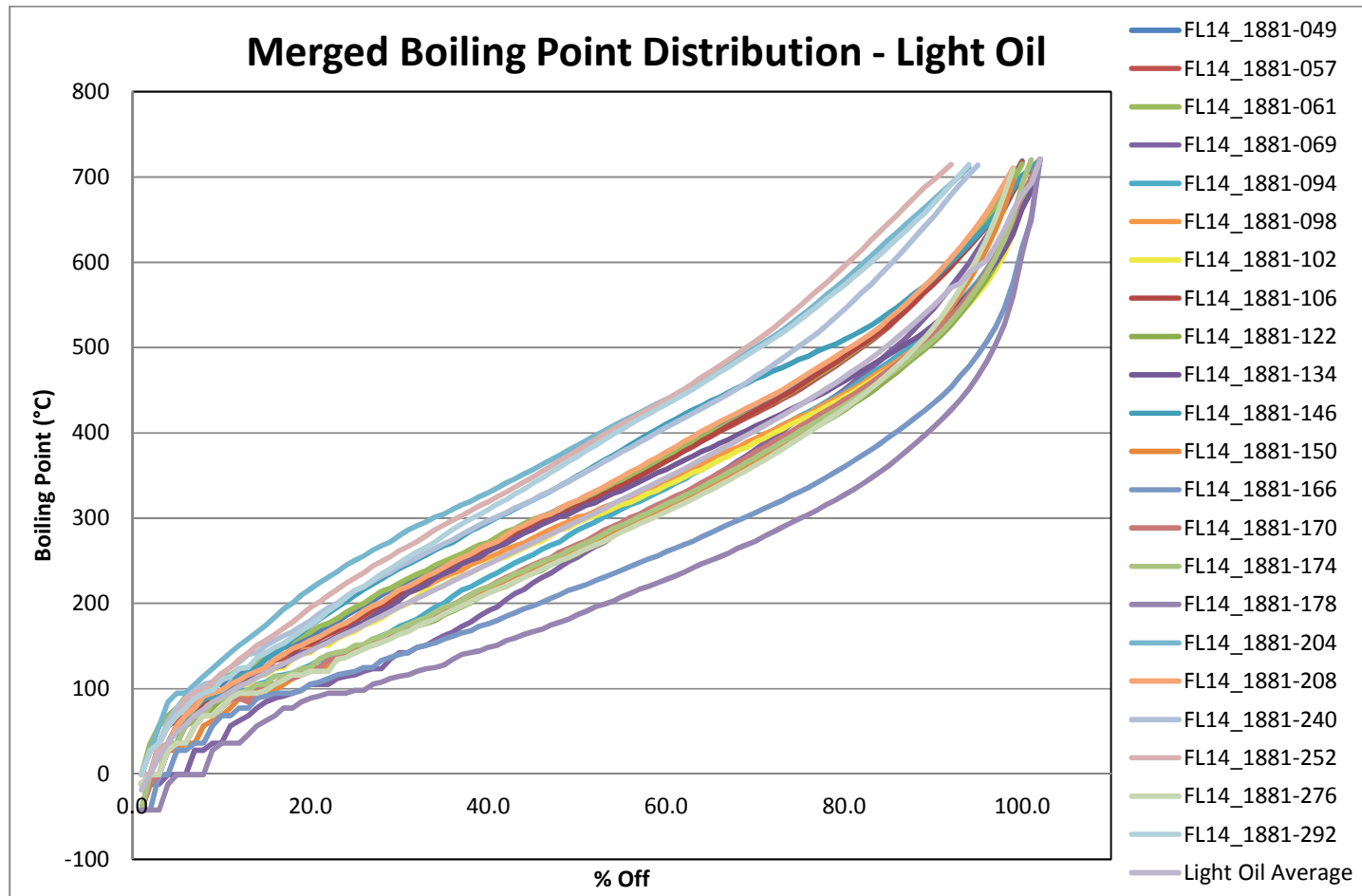


Figure 21: Light Oil Merged Boiling Point Distributions

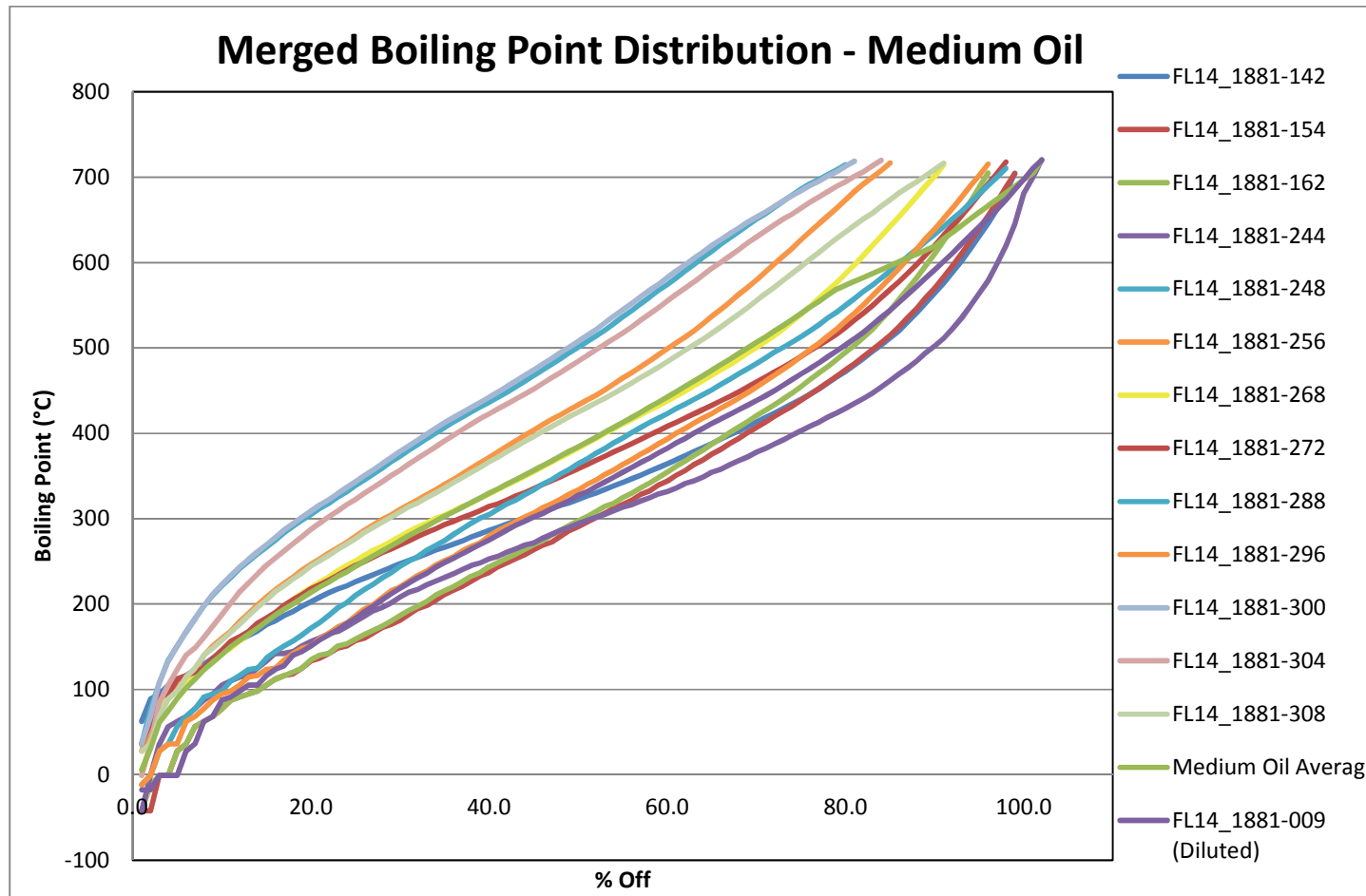


Figure 22: Medium Oil and Medium Diluted Oil Merged Boiling Point Distributions

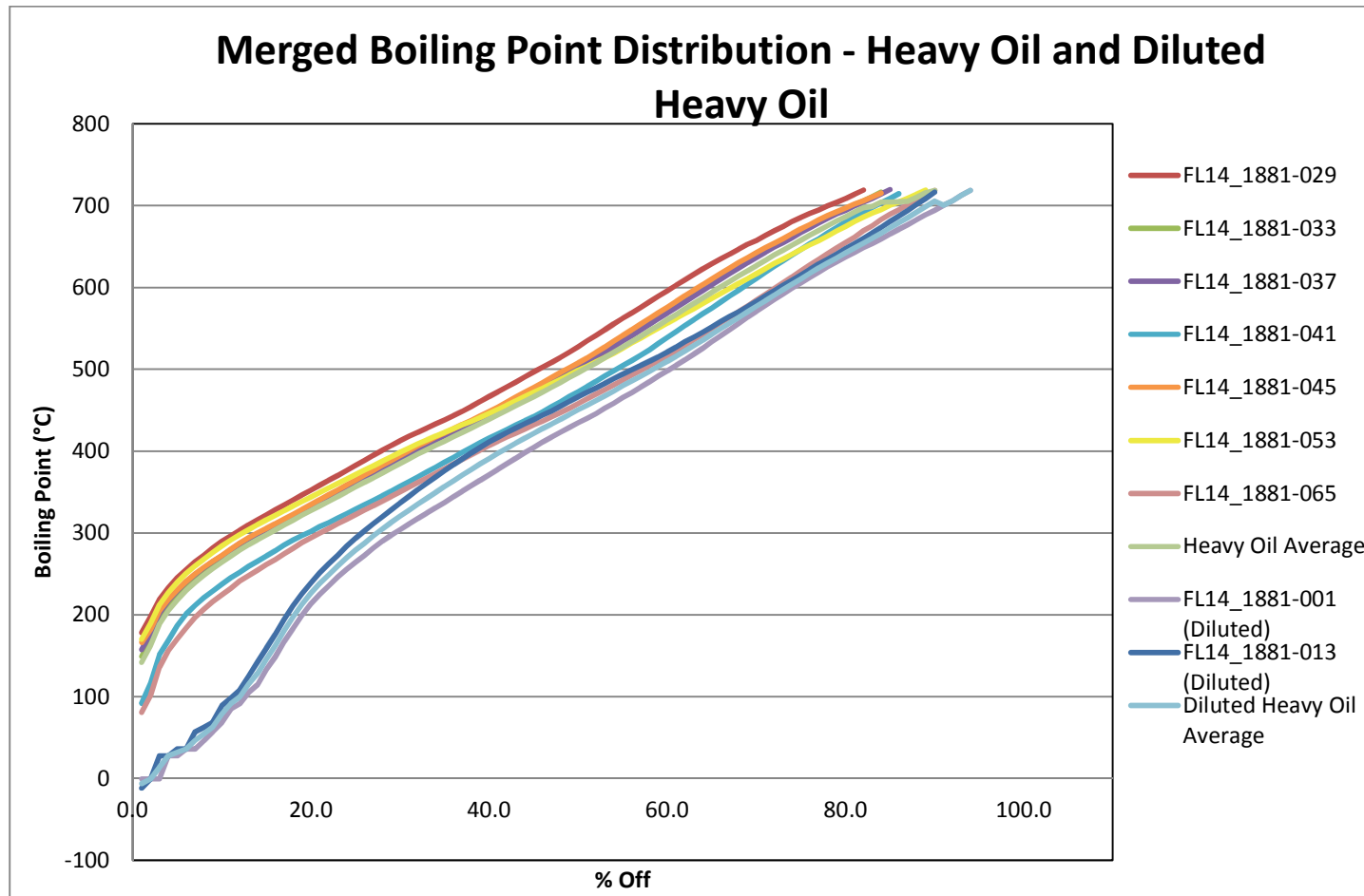


Figure 23: Heavy Oil and Diluted Heavy Oil Merged Boiling Point Distributions

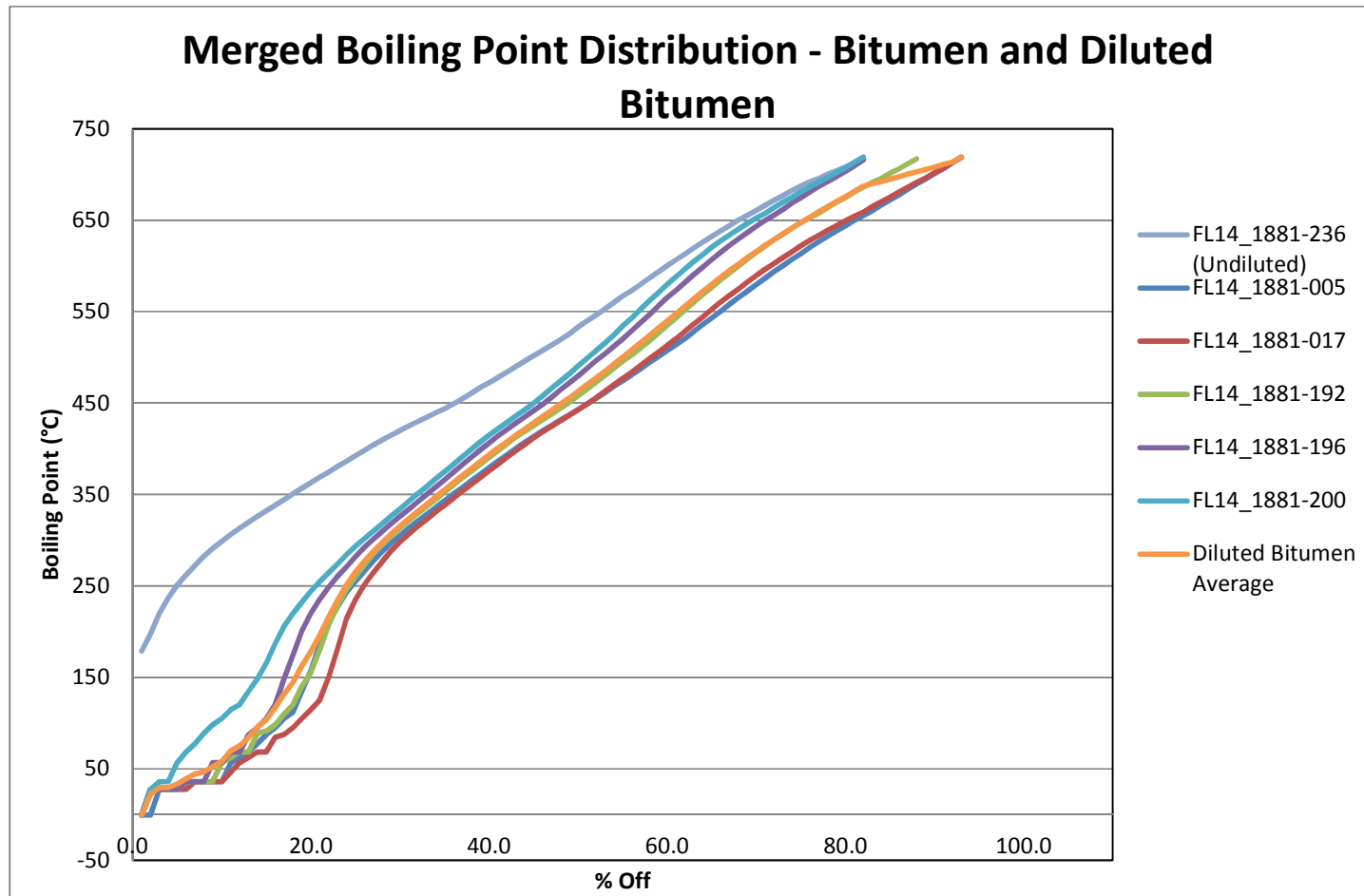


Figure 24: Bitumen and Diluted Bitumen (Dilbit) Merged Boiling Point Distributions



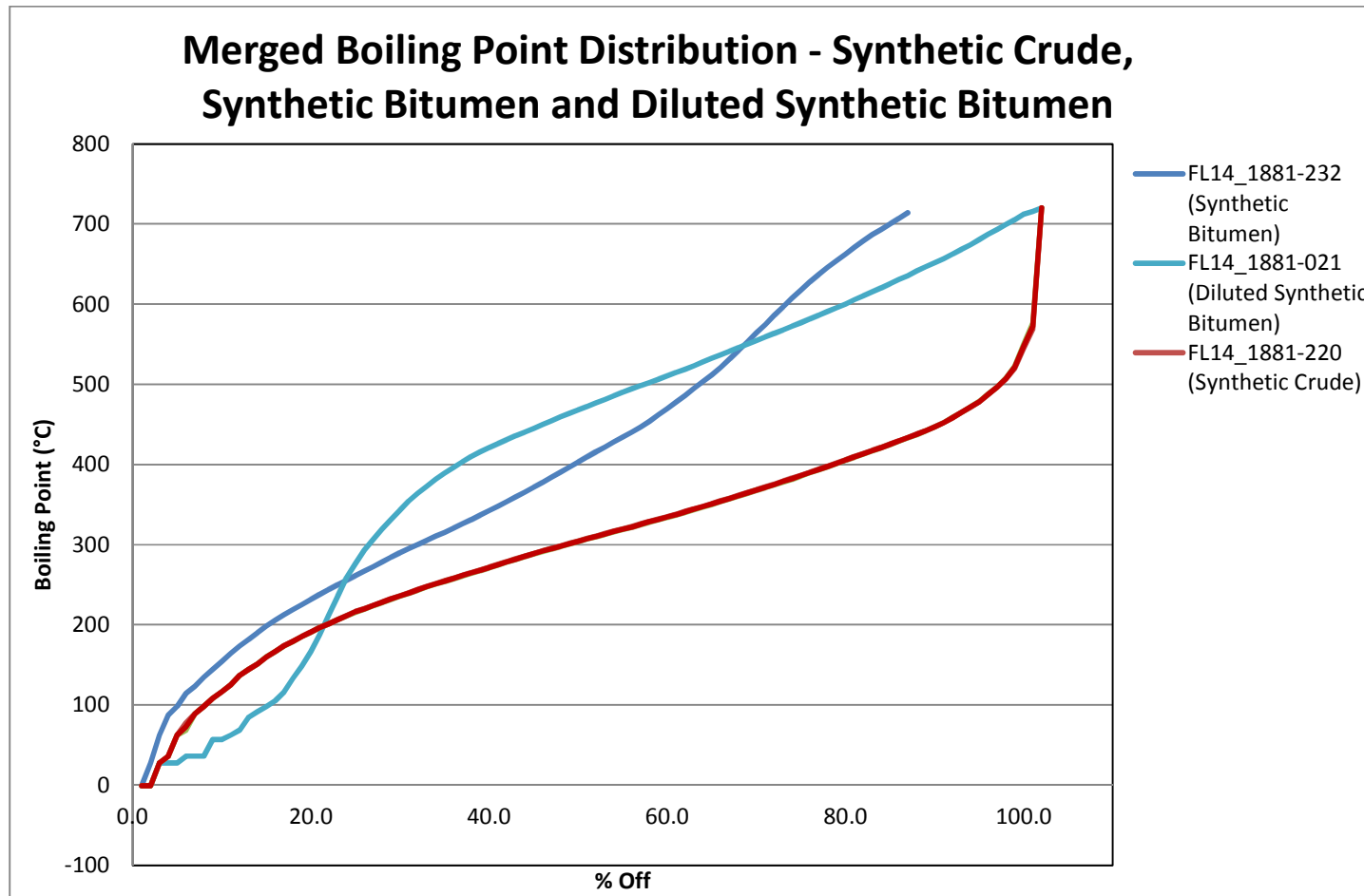


Figure 25: Synthetic Crude, Synthetic Bitumen (Synbit) and Diluted Synthetic Bitumen Merged Boiling Point Distribution

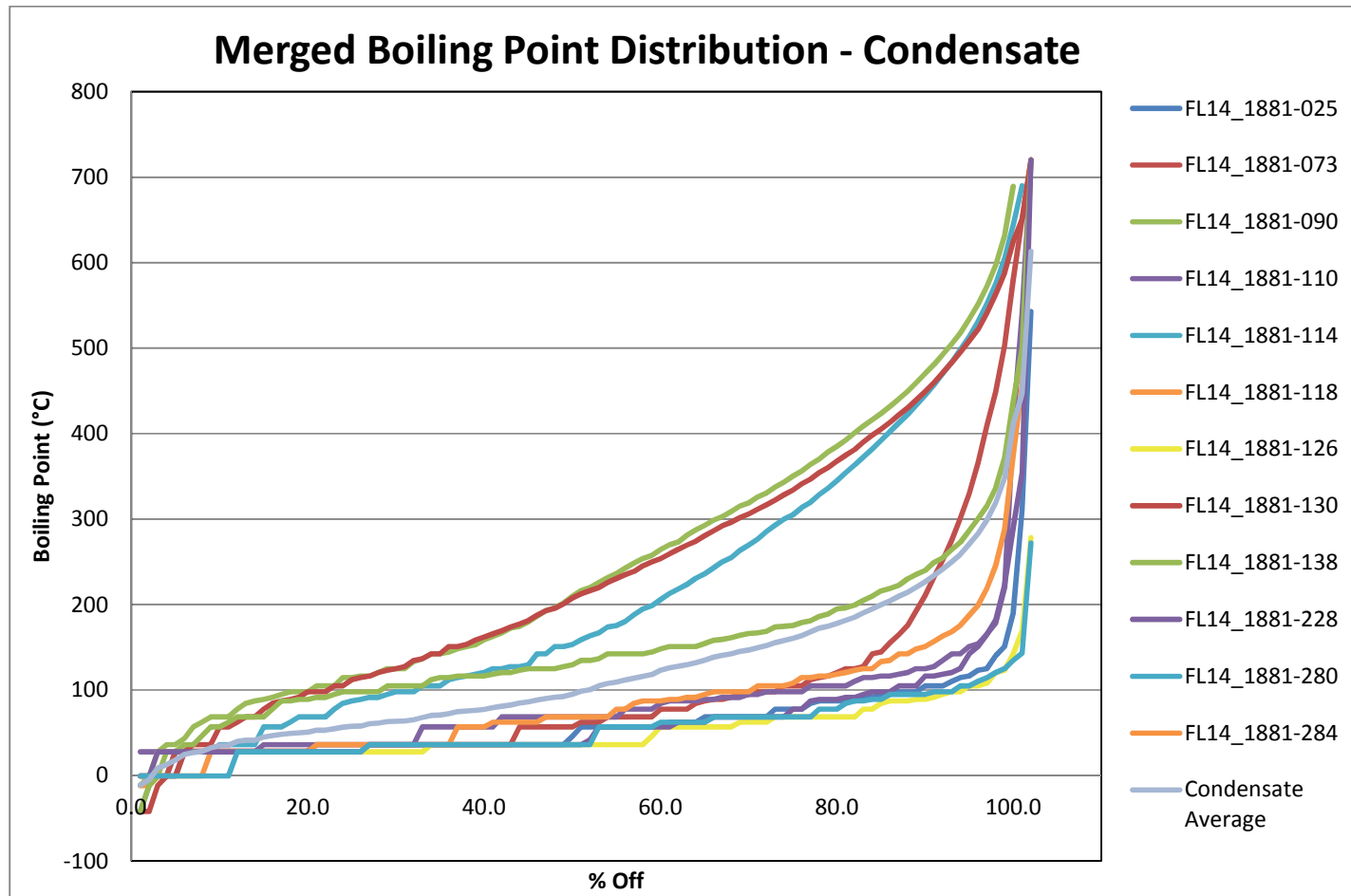


Figure 26: Condensate Merged Boiling Point Distributions

## 8.6 Initial Boiling Point

The initial boiling point (IBP) of all samples was determined by merged GC analysis, either ASTM D8003/ASTM D7169 or ASTM D7900/ASTM D7169. The IBP is the temperature at which 0.5 weight percent of the sample has eluted when determining the boiling range as defined in ASTM D7169 and API Recommended Practice 3000.

The IBP is determined from ASTM D8003 data in which individual components in the front end of the analysis (C1, C2, C3, iC4, nC5, iC5, neoC5, and nC5) are measured. Thus the initial boiling points will fall on one of these peaks, unless the IBP is over C5. A sample with an initial boiling point of  $-42.2^{\circ}\text{C}$  means that at 0.5 mass% off propane is being distilled off. The methane and ethane fractions will be distilled off before this. This number does not give an indication of how much methane and ethane the sample has, it also does not indicate how much propane the sample has, as this might be at the start of the propane peak or the end of a propane peak, or somewhere in the middle. Initial boiling point only indicates that 0.5% of the sample boils below  $-42.2^{\circ}\text{C}$  in these cases.

As an example, a sample with a boiling point of  $-11.7^{\circ}\text{C}$  means that the 0.5% distilled off will occur in the isobutene fraction. It might be the start end or middle of that fraction, simulated distillation does not tell us. A sample that has 0.75% iC4 and no methane, ethane and propane will have an IBP would be  $-11.7$ . However a sample with 0.45%propane,  $>0.05\%$  iC4 and no methane or ethane or a sample with 0.1% methane, 0.15% ethane, 0.2% propane and 0.3% iC4 will also have an IBP of  $-11.7$ . There is a multitude of scenarios that will result in the same IBP's.

The IBP was also determined using ASTM D86 for the samples in each region that contained the highest proportion of light ends. The initial boiling point (IBP) is reported as the corrected temperature reading at the instant the first drop of condensate falls from the lower end of the condenser tube. ASTM D86 is not sensitive to non-condensable components (C1 to C3), therefore the reported IBP will not reflect their presence or absence in a sample. As well, since the distillation is performed under atmospheric conditions, there are evaporative losses of light ends. The average IBP by crude type and the comparison between the two methods is shown below in Figure 27 and Tables 10 and 11.

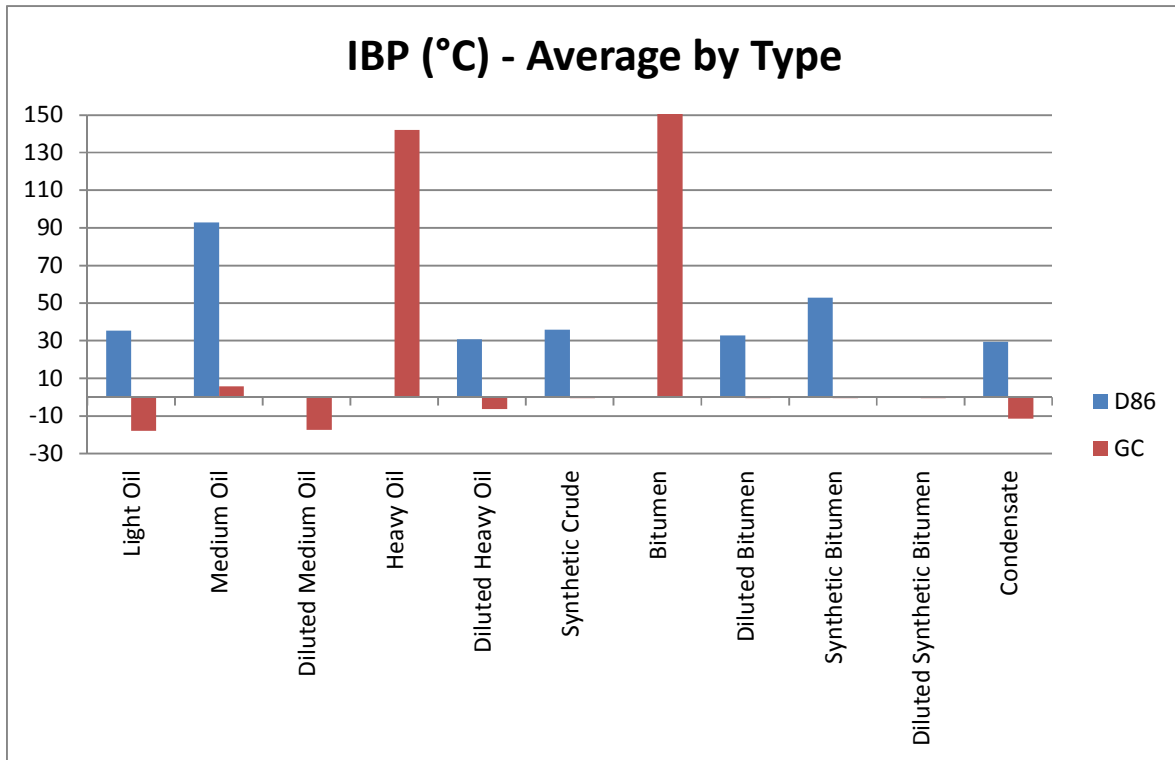


Figure 27: Average IBP by Crude Oil Type as Determined by GC and ASTM D86

Table 10: Difference in IBP – Average by Type

Sample Type	Average IBP (°C), ASTM D86	Average IBP (°C), ASTM D8003/ASTM D7169	Average Δ (°C)
Light Oil	35.3	-17.9	53.2
Medium Oil	92.8*	62.4*	30.4*
Diluted Heavy Oil	30.9	-6.2	37.1
Synthetic Crude	35.8	-0.6	36.4
Diluted Bitumen	32.9	-0.6	33.5
Synthetic Bitumen	52.8	-0.6	53.4
Condensate	29.3	-11.4	40.7

\*Single value as only one medium oil was submitted for ASTM D86.

# ANNEX B - AITF REPORT (EN)



Table 11: Difference in IBP – Individual Samples

LIMs #	Region	Sample Type	IBP (°C), ASTM D86	IBP (°C), ASTM D8003/ASTM D7169	Δ(°C)
FL14_1881-025	AB	condensate	29.4	-0.6	30
FL14_1881-073	AB	condensate	28.4	-0.6	29
FL14_1881-114	B.C.	condensate	27.6	-42.2	69.8
FL14_1881-118	B.C.	condensate	26.6	-11.7	38.3
FL14_1881-126	B.C.	condensate	30.8	-0.6	31.4
FL14_1881-138	B.C.	condensate	36.6	-42.2	78.8
FL14_1881-228	AB	condensate	28.1	-0.6	28.7
FL14_1881-280	ND	condensate	23.9	-0.6	24.5
FL14_1881-284	ND	condensate	25.2	-11.7	36.9
FL14_1881-110	B.C.	condensate, sour	36.1	27.8	8.3
FL14_1881-005	AB	dilbit	29.7	-0.6	30.3
FL14_1881-017	AB	dilbit	30.7	-0.6	31.3
FL14_1881-192	AB	dilbit	31.4	-0.6	32
FL14_1881-200	AB	dilbit	39.8	-0.6	40.4
FL14_1881-001	AB	heavy oil, diluted	30.9	-0.6	31.5
FL14_1881-049	SK	light oil	48.8	-0.6	49.4
FL14_1881-057	SK	light oil	44.4	-0.6	45
FL14_1881-122	B.C.	light oil	33	-42.2	75.2
FL14_1881-146	MB	light oil	33.6	-42.2	75.8
FL14_1881-150	MB	light oil	28.5	-42.2	70.7
FL14_1881-166	SK	light oil	30.3	-42.2	72.5
FL14_1881-178	SK	light oil	28.2	-42.2	70.4
FL14_1881-240	AB	light oil	45.7	-0.6	46.3
FL14_1881-276	MB	light oil	35.8	-11.7	47.5
FL14_1881-069	AB	light oil, sour	28.1	-11.7	39.8
FL14_1881-106	B.C.	light oil, sour	32.3	-11.7	44
FL14_1881-170	SK	light oil, sour	30.7	-42.2	72.9
FL14_1881-174	SK	light oil, sour	34.5	-42.2	76.7
FL14_1881-292	AB	light oil, sour	44.7	-0.6	45.3
FL14_1881-142	MB	medium oil	92.8	62.4	30.4
FL14_1881-232	AB	syn-bit	52.8	-0.6	53.4
FL14_1881-220	AB	synthetic crude	36.4	-0.6	37
FL14_1881-224	AB	synthetic crude	35.2	-0.6	35.8
<b>Average Δ</b>					<b>46.3</b>

Sample FL14\_1881-110 had the highest initial boiling point of all the condensates, 27.8°C, as determined by GC analysis. Only 0.2 mass % of the sample was below C5 which has a boiling point of 36.1°C. As a result, the light end loss during ASTM D86 would be minimal and the difference between the two methods was small. The percentage of C1 to C4 components in a condensate will vary depending on the temperatures and pressures used in the separation and stabilization processes.

As shown in Table 12, the IBP determined by ASTM D86 was consistently higher than the IBP determined by GC analysis. The difference in IBP between the two methods ranged from 8°C to 79°C, with an average difference of 46.3°C. Based on the results observed, the most accurate method for determining IBP is the GC merge method in which the ASTM D8003 data is merged with the ASTM D7169 data. The use of ASTM D86 to determine IBP can be criticized for many reasons; the method gives biased IBP results, the results can vary depending on the method parameters chosen and it was not developed for samples with a wide boiling range.

ASTM D86 is a distillation performed at atmospheric pressure. Light end loss occurs due to the following factors: evaporation during the sampling process, evaporation during transfer from the sample container to the distillation flask, vapour loss during the distillation and distillation loss due to non-condensable light ends (methane, ethane, propane) at the D86 conditions. The loss of the light ends results in an IBP higher than the sample composition would indicate.

The IBP can also be affected by group selection. Based on its composition, vapour pressure, expected IBP or a combination of these properties, a sample is placed in one of four groups. The assignment of a sample to a specific group affects the storage and conditioning temperature of the sample and the heating rate during distillation. For example Group 1 requires the sample to be conditioned to below 10°C, the flask temperature at the start of the test to be 13-18°C and it has the slowest heating rate whereas Group 4 requires the sample to be conditioned at ambient temperature, the flask temperature at the start of the test to be at ambient and it has the fastest heating rate. The same sample will have a different IBP depending on the group chosen. Sample FL14\_1881-003 was run using Group 4 then Group 1 and the IBP was determined to be 35.4°C and 30.9° respectively. As the cut off between packing group I and II is 35°C, this could have affected the assignment of the packing group.

ASTM D86 was designed for the analysis of distillate fuels and it is not applicable to products containing appreciable quantities of residual material. A complete distillation profile cannot be obtained for samples heavier than condensates as the samples will either bump or thermally crack. The IBP can still be determined for these types of samples but the run must be

---

continuously monitored and stopped before the samples bumps or cracks. A complete distillation profile was obtained for all condensate samples except one, FL14\_1881-116. This sample was the heaviest of the condensates submitted for ASTM D86, with a C25+ fraction of 13.7%, which was too high to obtain a complete distillation profile. The light crude runs had to be stopped due to a “drops per volume” alarm. This alarm occurs when the sample has started to distill and the heating rate of the sample does not keep up with the distillation rate within the parameters of the method. This terminates the test. The dilbit and synthetic crude runs had to be stopped to prevent the samples from bumping. Bumping of the sample occurs when the sample heats up too fast in an effort to meet the specified distillation rate.

The distillation of a dilbit sample, FL14\_1881-007, is shown below in Figure 28. At this point in the distillation, the light ends have been evaporated off. Heating of the sample continues and since the sample is under atmospheric pressure, the heavier ends start to thermally crack and produce smoke observed in the picture. In order to distill the heavier ends, distillation under vacuum would be required. The brown colored liquid running down the side of the graduated cylinder is the paraffins in the sample.



Figure 28: ASTM D86 Distillation of a Dilbit, FL14\_1881-007



## 8.7 C1 to C24 Composition: Merging of ASTM D8003/ASTM D7169 or ASTM D7900/ASTM D7169 Data

The chemical composition in mass % up to C24 of each sample was determined by merging the data from two gas chromatography methods; either ASTM D8003 or ASTM D7900 with ASTM D7169. The portion of the sample above C24 is reported as C25+ residue. The average C1 to C24 and C1 to C8 compositions of each oil are shown in Figures 29 to 36. The average C25+ residues are shown in Figure 37.

As the density of the undiluted samples increases, from light oil to bitumen, the amount of light ends (C1 to C8) decreases and the amount of heavier ends increases, as can be seen in Figures 29 and 30. Light oils have the largest amount of hydrocarbons in the range C4 to C8 and smallest amount in the range of C11 to C24 while the bitumen shows the opposite composition. As a result, the C25+ residue (Figure 35) increases for the undiluted samples as the samples get heavier, from light oil (33.5%) to bitumen at (75.9%). Decreasing concentrations of light ends will result in higher flash points and lower vapour pressures.

Condensates are largely composed of hydrocarbons in the range C4 to C8 with very little C25+ residue (5.6%) as can be seen in Figures 31, 32 and 35. The effect of adding condensate as a diluent on the composition of heavy oil and bitumen can be seen in Figures 33, 34 and 37. Whereas the undiluted heavy oil and bitumen have very low concentrations of hydrocarbons in the range of C1 to C8, the composition of the diluted oils in the range of C1 to C8 closely resembles that of condensate. The diluted bitumen has a greater concentration of hydrocarbons in this region than diluted heavy oil as more diluent is required for bitumen than heavy oil. The diluted heavy oils and bitumen also have a lower amount of C25+ residue than their undiluted counterparts. The light ends compositions of the diluted samples will result in lower flash points and higher vapour pressures than the undiluted samples.

Synthetic crude is produced by partially upgrading bitumen is a blend of naphtha, distillate and gas oil range materials, with no residuum. This composition is evident in figures 35 and 36, which show a much higher concentration of hydrocarbons in the range C1 to C24 than bitumen with the most significant difference in the C1 to C8 region. The amount of C25+ residue for synthetic crude, 25.4%, is much lower than that for bitumen, 75.9%.

The effect of adding synthetic crude to bitumen to produce synthetic bitumen and adding condensate to synthetic bitumen to produce diluted synthetic bitumen is shown in Figures 35, 36 and 37. The C1 to C8 range of the synthetic bitumen resembles the synthetic crude and the C25+ residue of the synthetic bitumen (52.6%) is higher than the synthetic crude (24.2%) but

lower than bitumen (75.9%). The diluted synthetic bitumen composition clearly shows the contribution from condensate in the hydrocarbon range C4 to C6, which makes up the largest portion of the condensate composition. The C25+ residue of the diluted synthetic bitumen (65.4%) is lower than that of bitumen (75.9%).

The C25+ residue of the diluted synthetic bitumen (65.4%) was higher than that of the synthetic bitumen (52.6%) which is opposite of what might be expected. However, it should be noted that the values for synthetic bitumen and diluted synthetic bitumen are single sample values not averages. The samples are also from separate sources, which means that a different synthetic crude and/or bitumen may have been used.

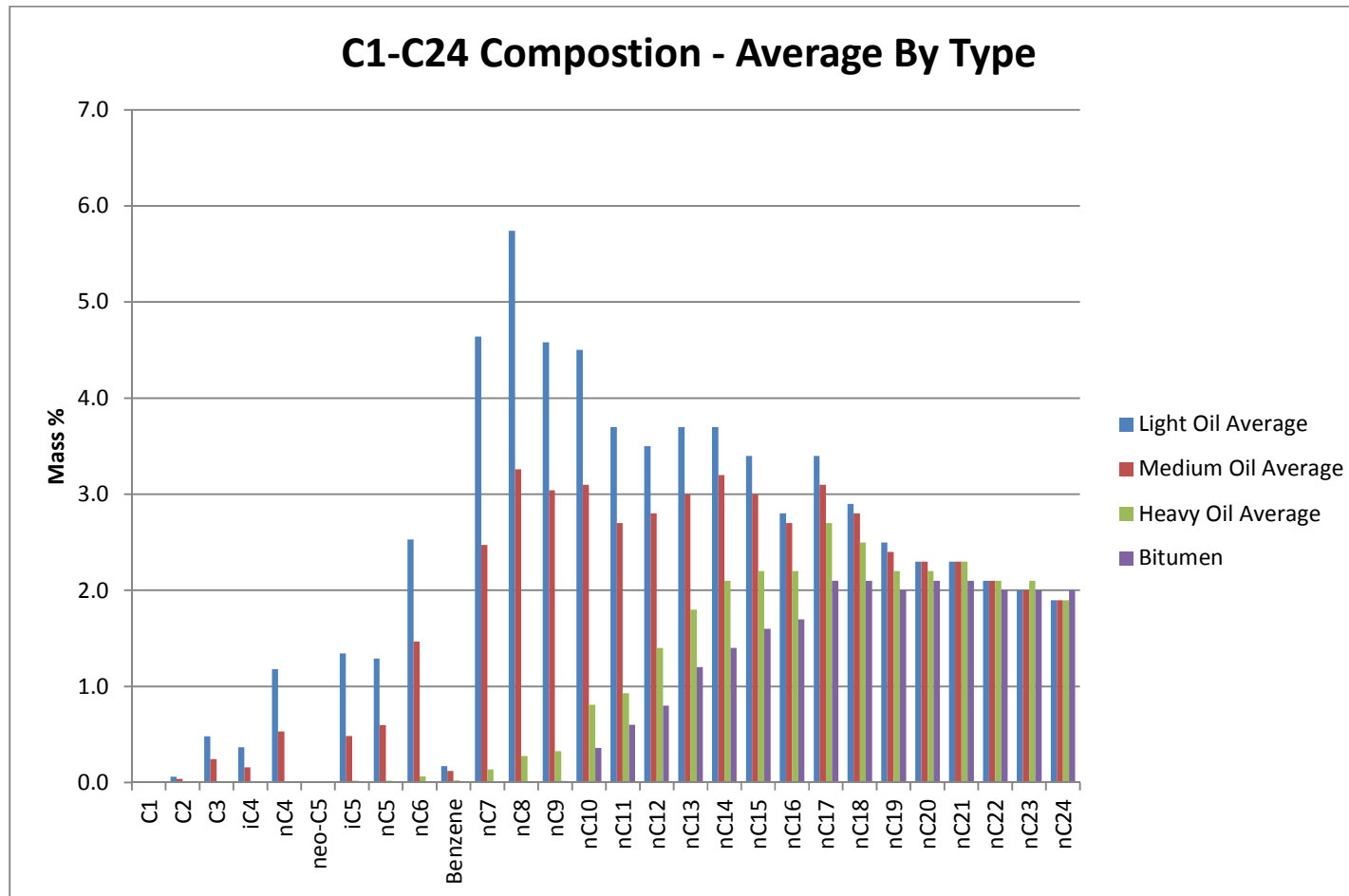


Figure 29: Average C1 to C24 Composition of Light Oil, Medium Oil, Heavy Oil and Bitumen

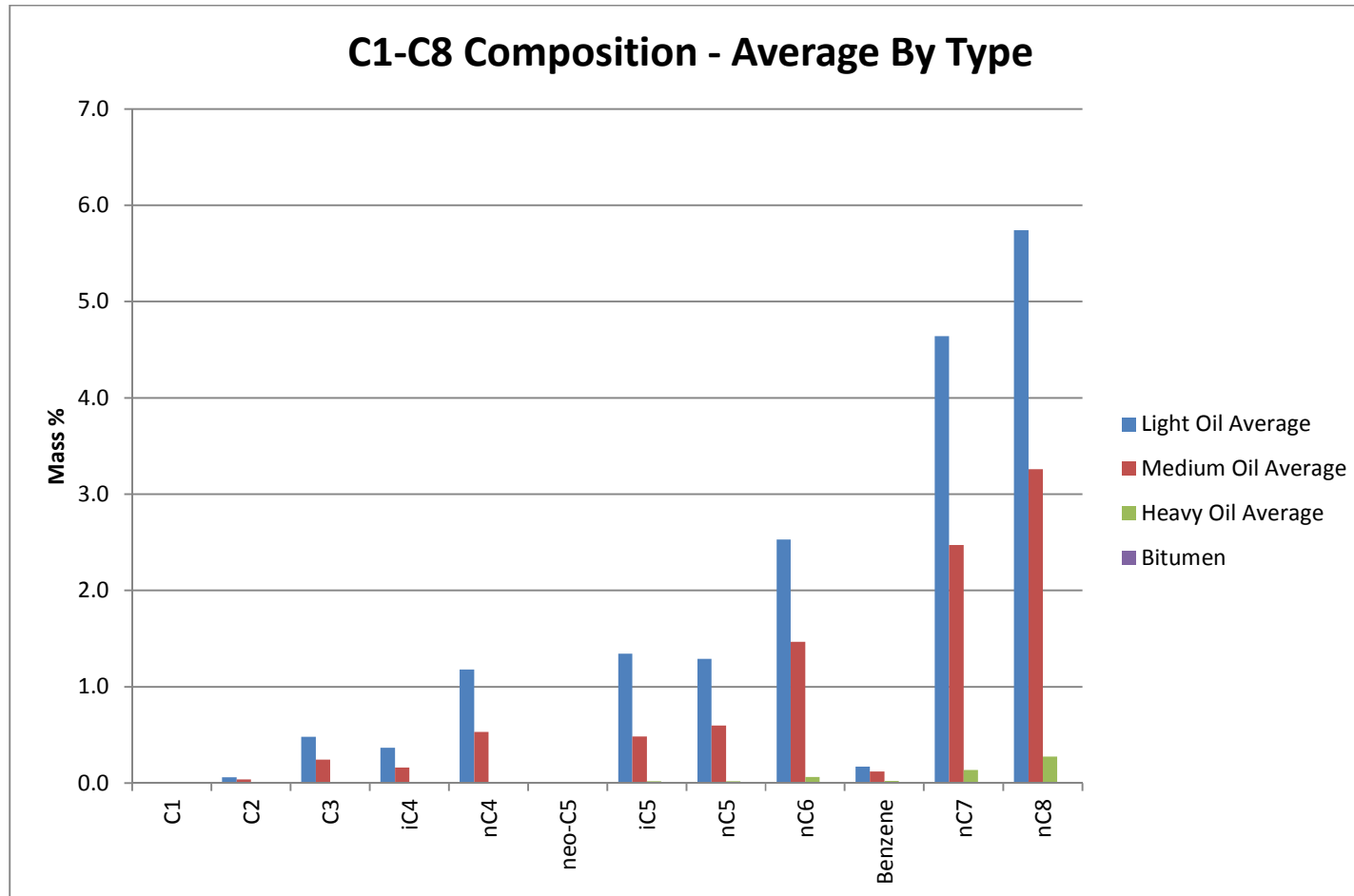


Figure 30: Average C1 to C8 Composition of Light Oil, Medium Oil, Heavy Oil and Bitumen

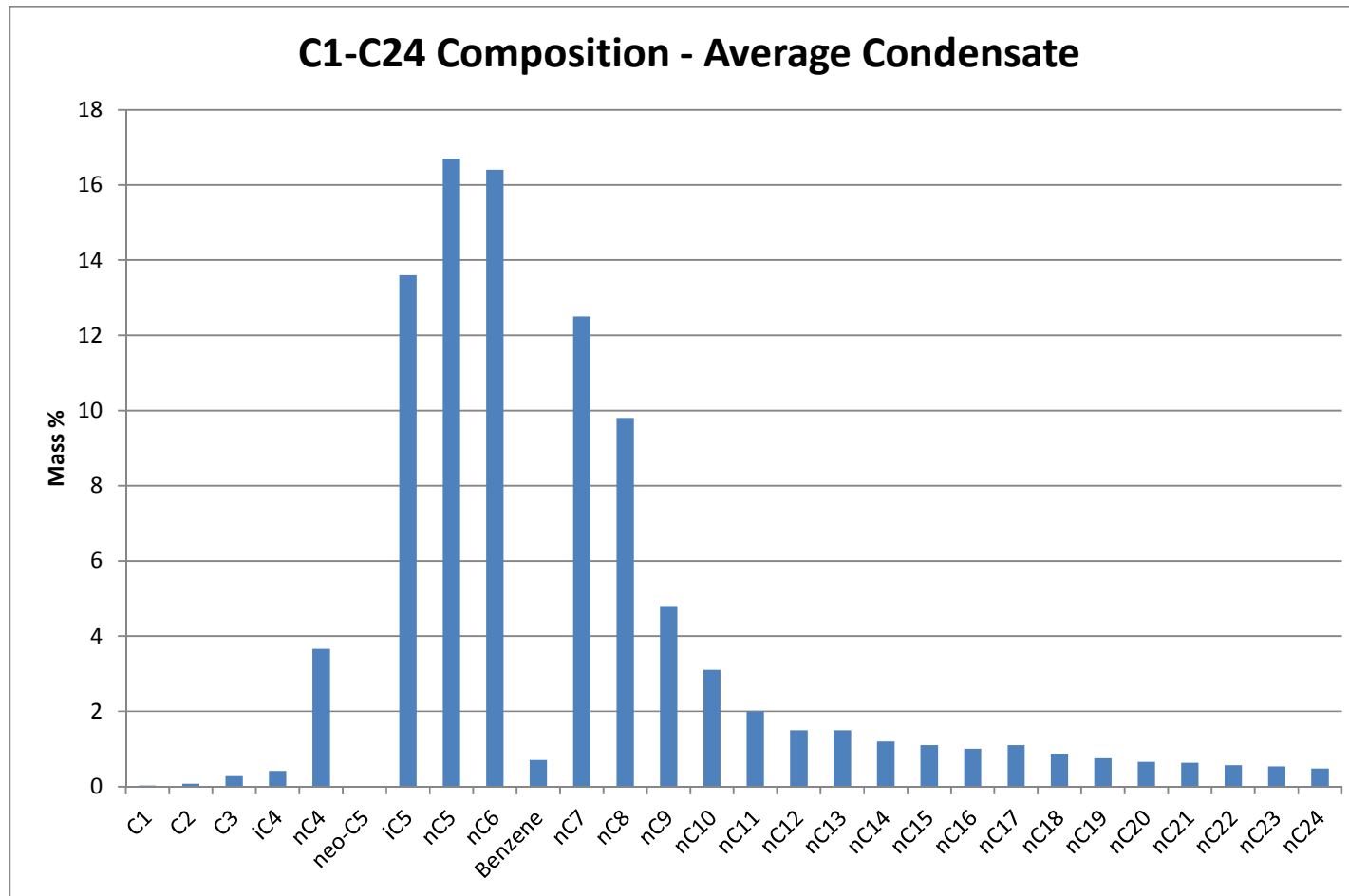


Figure 31: Average C1 to C24 Composition of Condensate

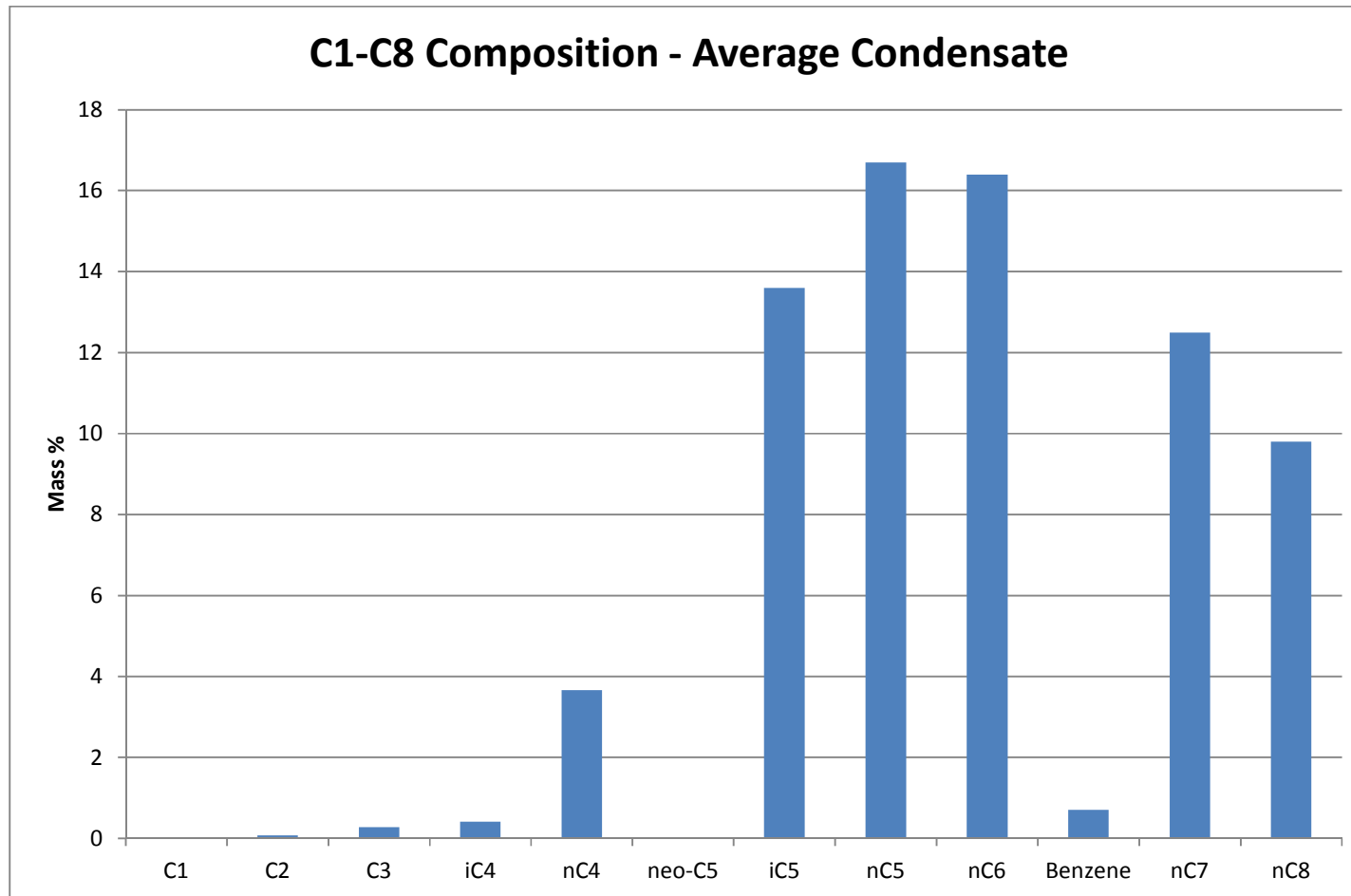


Figure 32: Average C1 to C8 Composition of Condensate

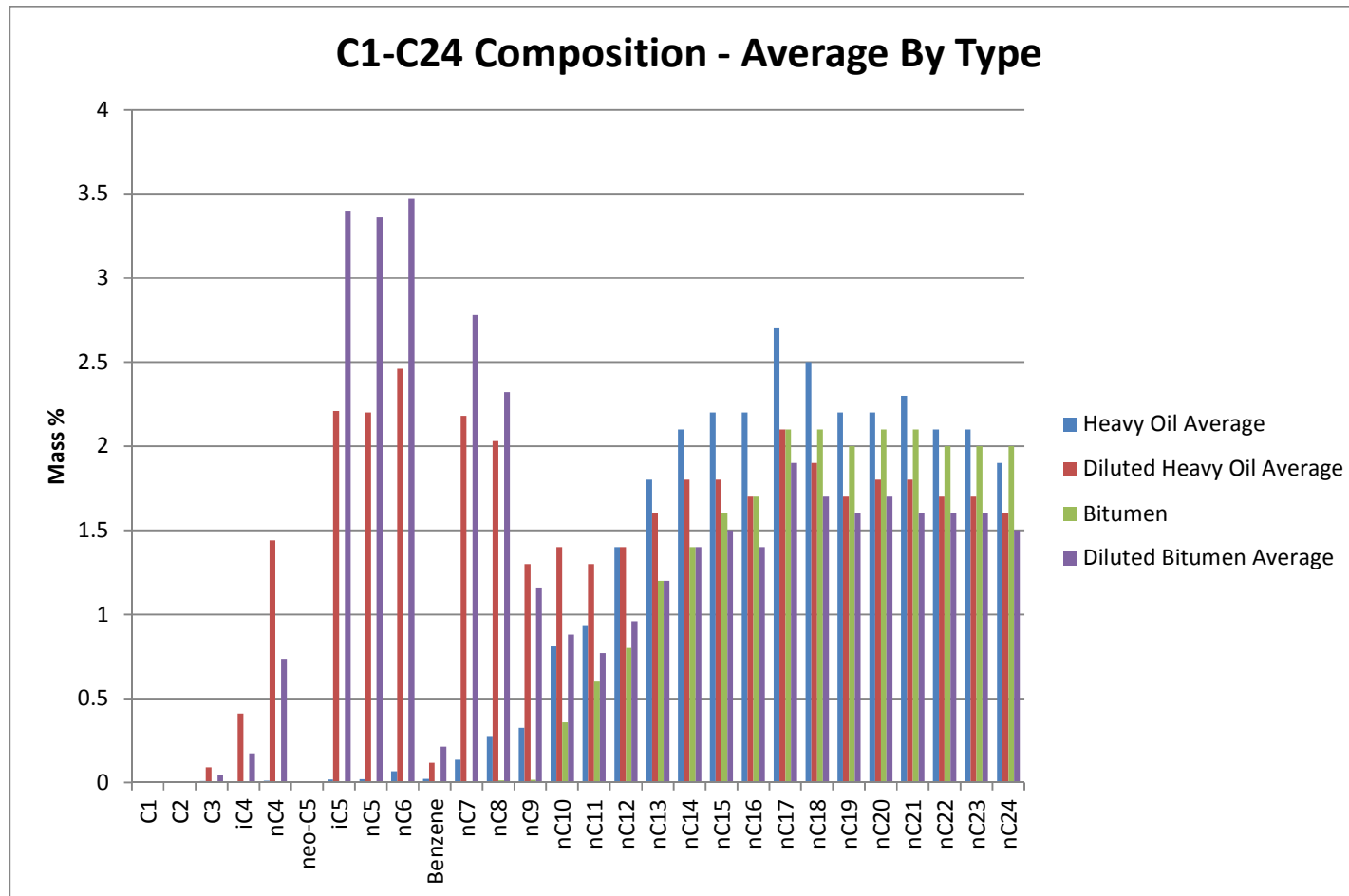


Figure 33: Average C1 to C24 Composition of Heavy Oil, Diluted Heavy Oil, Bitumen and Diluted Bitumen

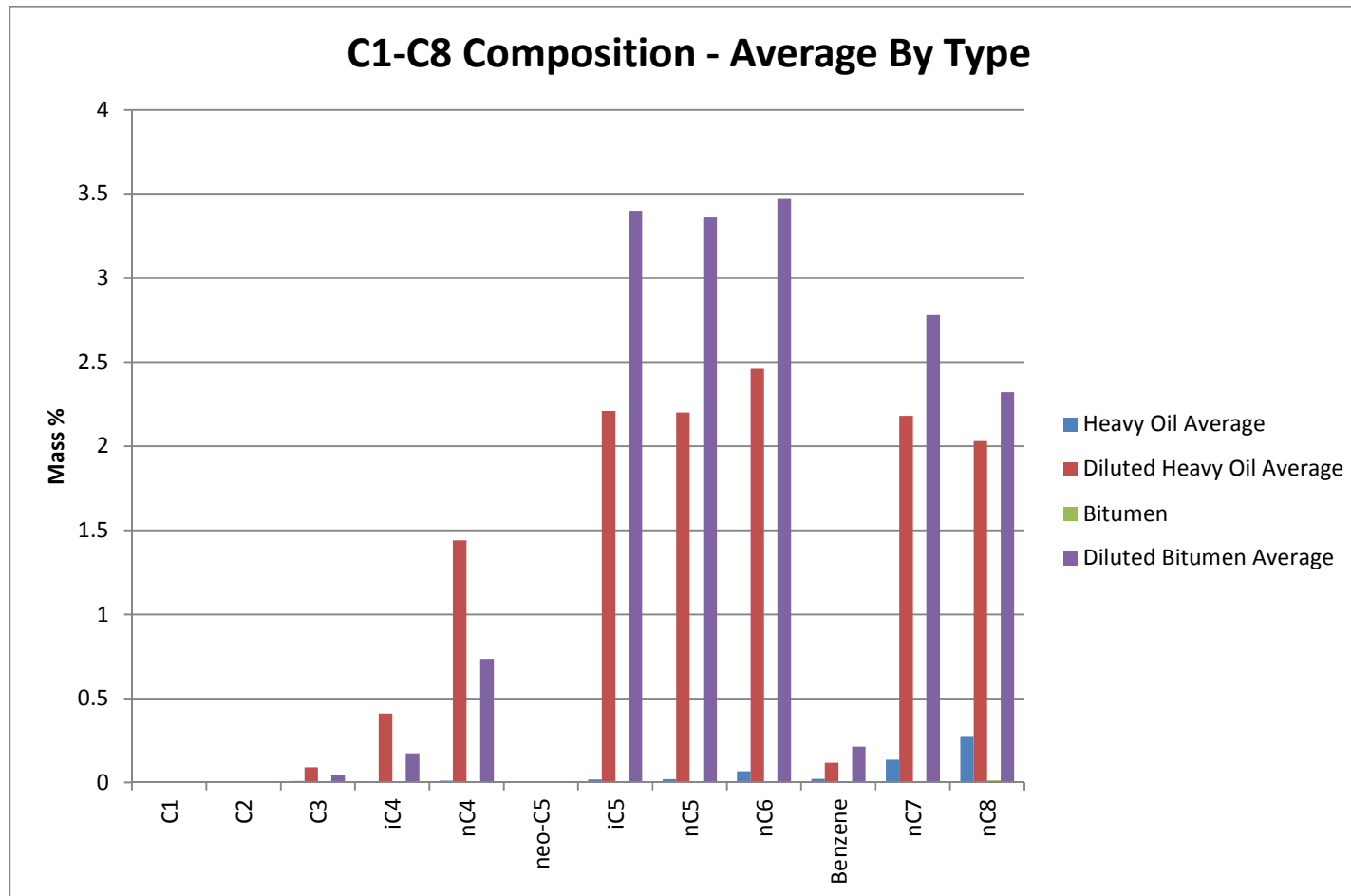


Figure 34: Average C1 to C8 Composition of Heavy Oil, Diluted Heavy Oil, Bitumen and Diluted Bitumen



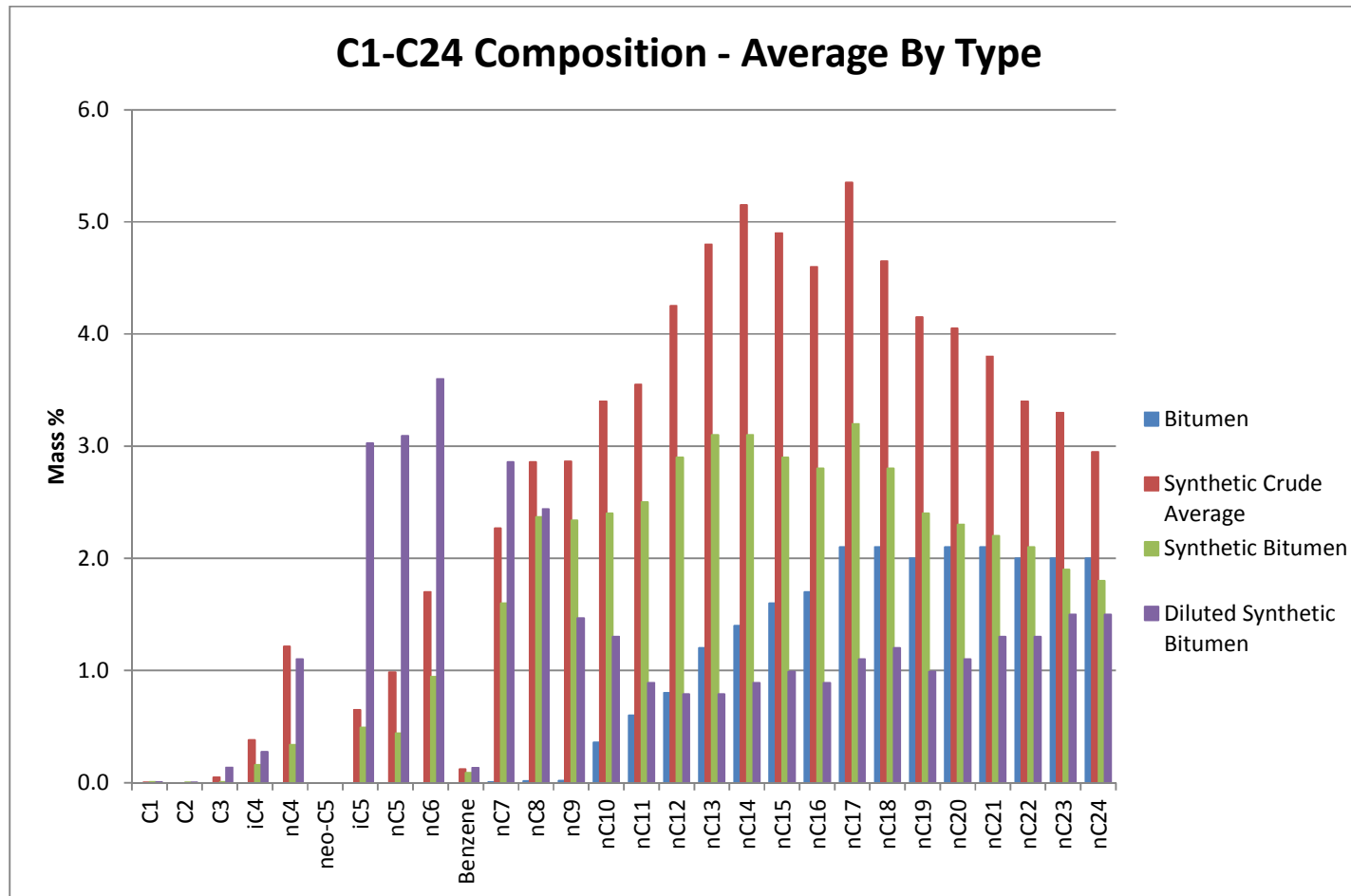


Figure 35: Average C1 to C24 Composition of Bitumen, Synthetic Crude, Synthetic Bitumen, and Diluted Synthetic Bitumen

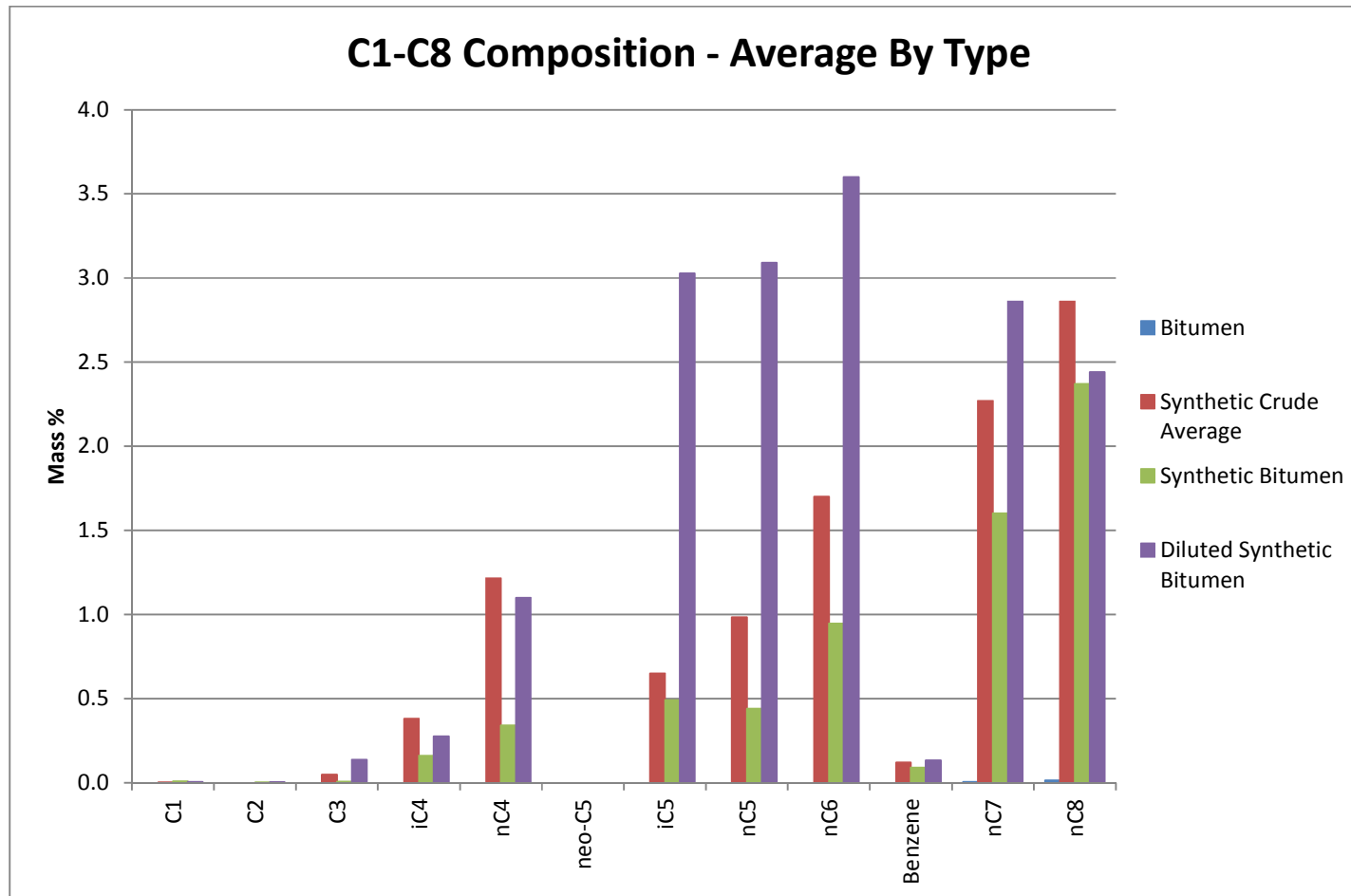


Figure 36: Average C1 to C8 Composition of Bitumen, Synthetic Crude, Synthetic Bitumen, and Diluted Synthetic Bitumen

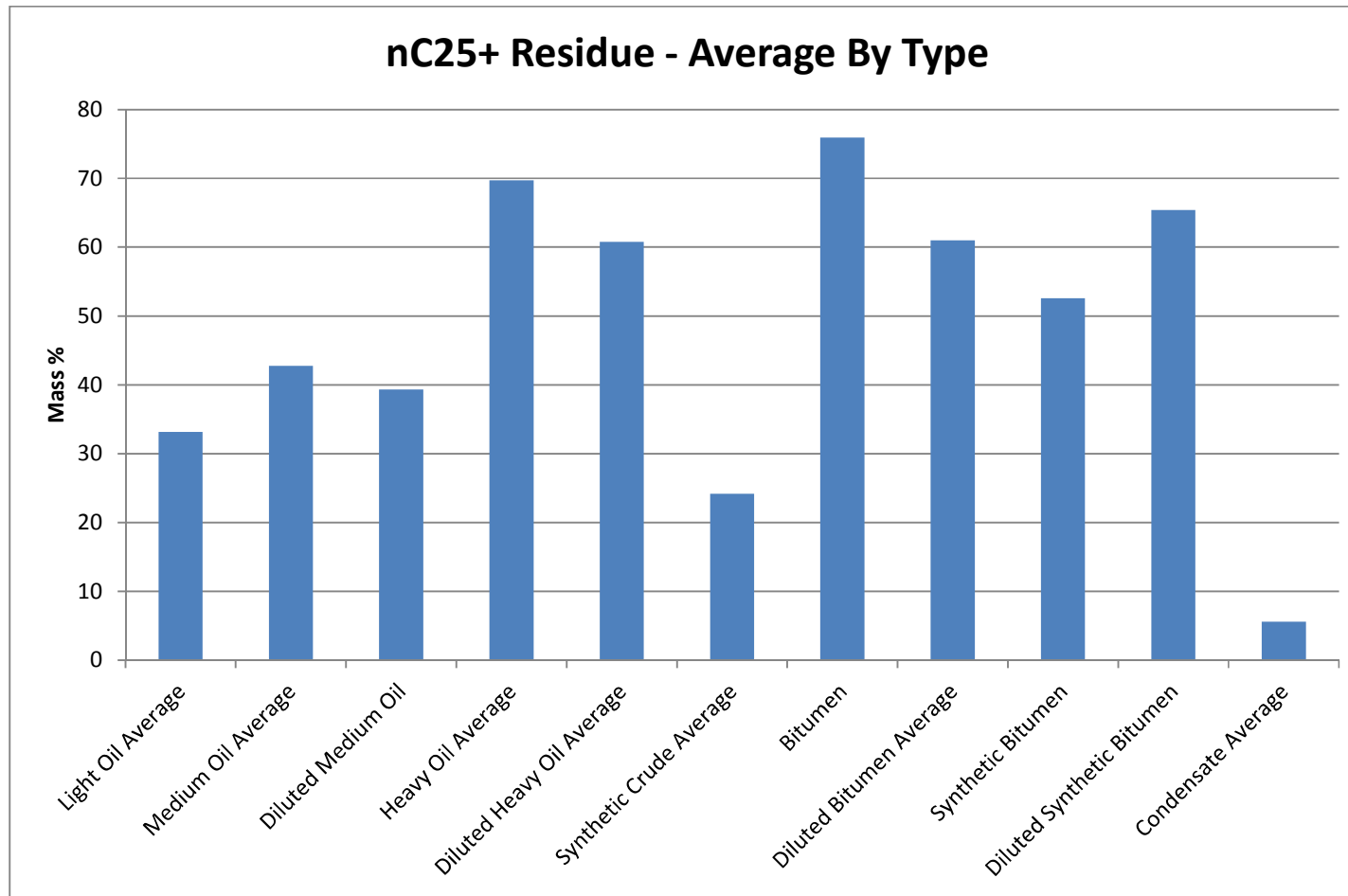


Figure 37: Average C25+ Residue of All Crude Types

## ANNEX B - AITF REPORT (EN)



---

For each type of oil, two additional graphs were prepared: the C1 to C24 composition of the average and two samples at either end of the spectrum, and the C1 to C8 composition of the average and the samples at either end of the spectrum. These graphs, seen in Figures 38 to 51, demonstrate the amount of variation within each oil type and specifically the variation in the composition of the light ends. The variation is to be expected as the samples were collected from different geographic regions and from different points in the transportation chain. As well, the definitions of each oil type are based on API gravity cut offs not composition which will result in variability within each type of oil.

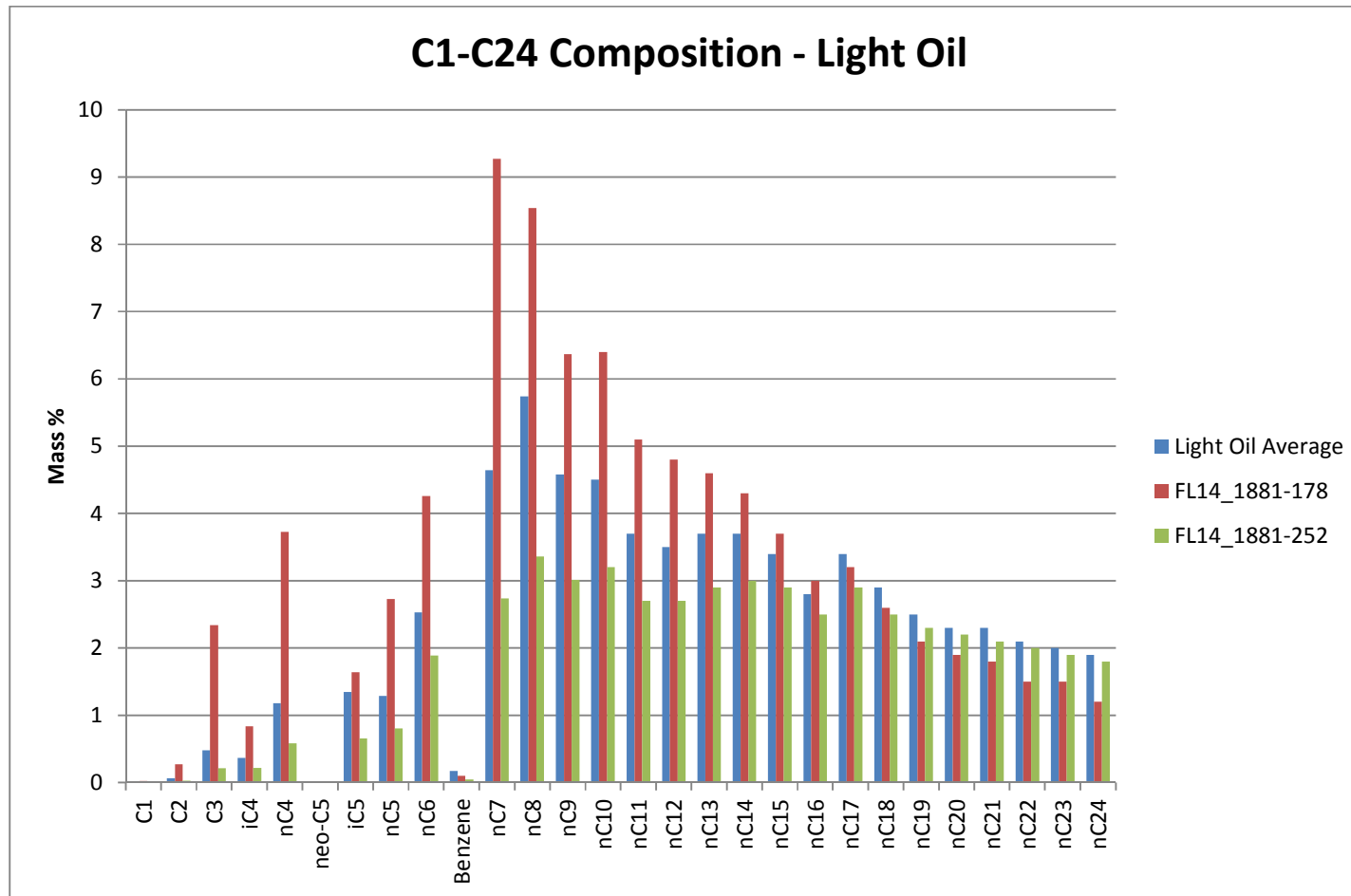


Figure 38: Light Oil C1 to C24 Composition

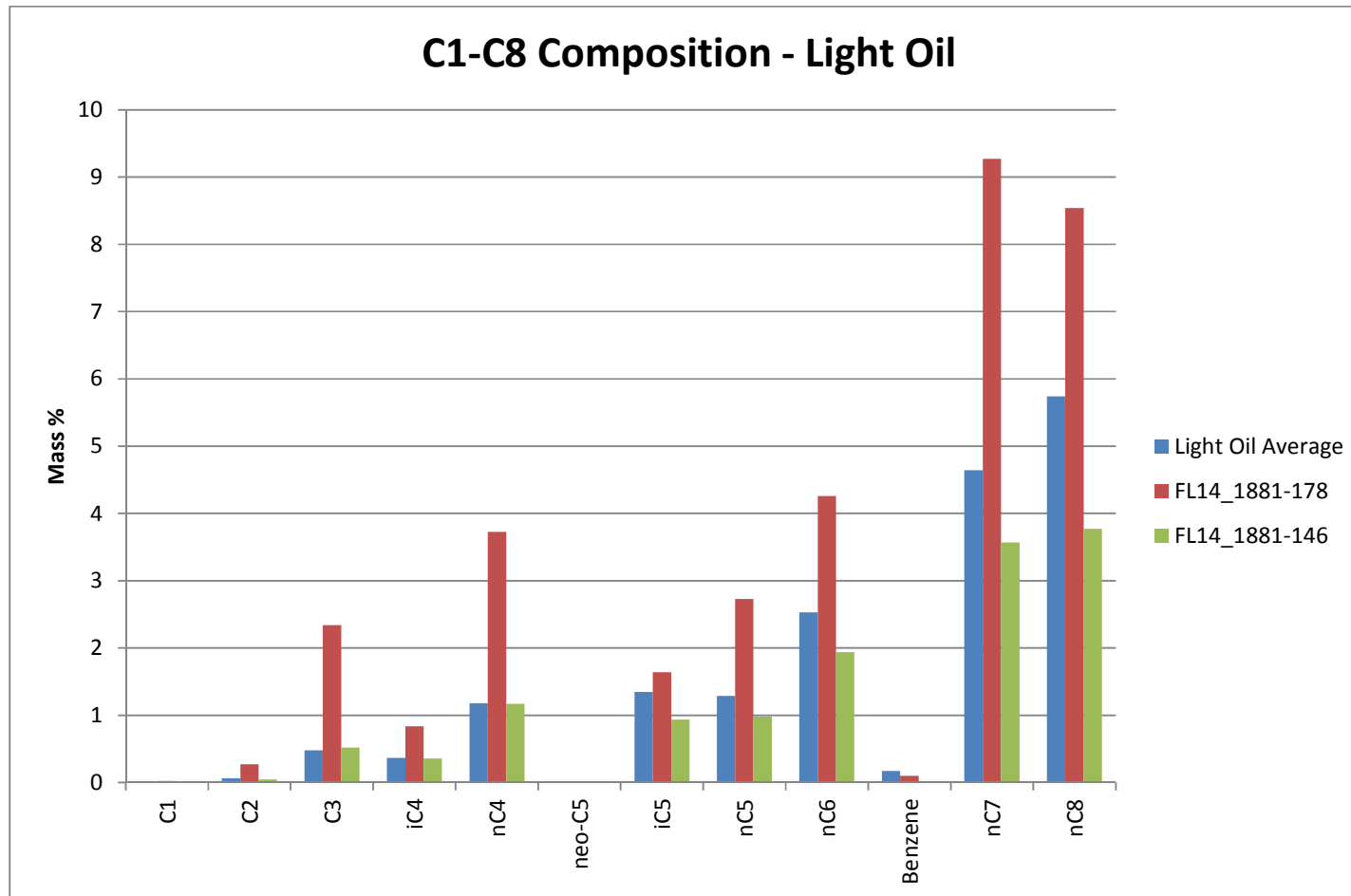


Figure 39: Light Oil C1 to C8 Composition

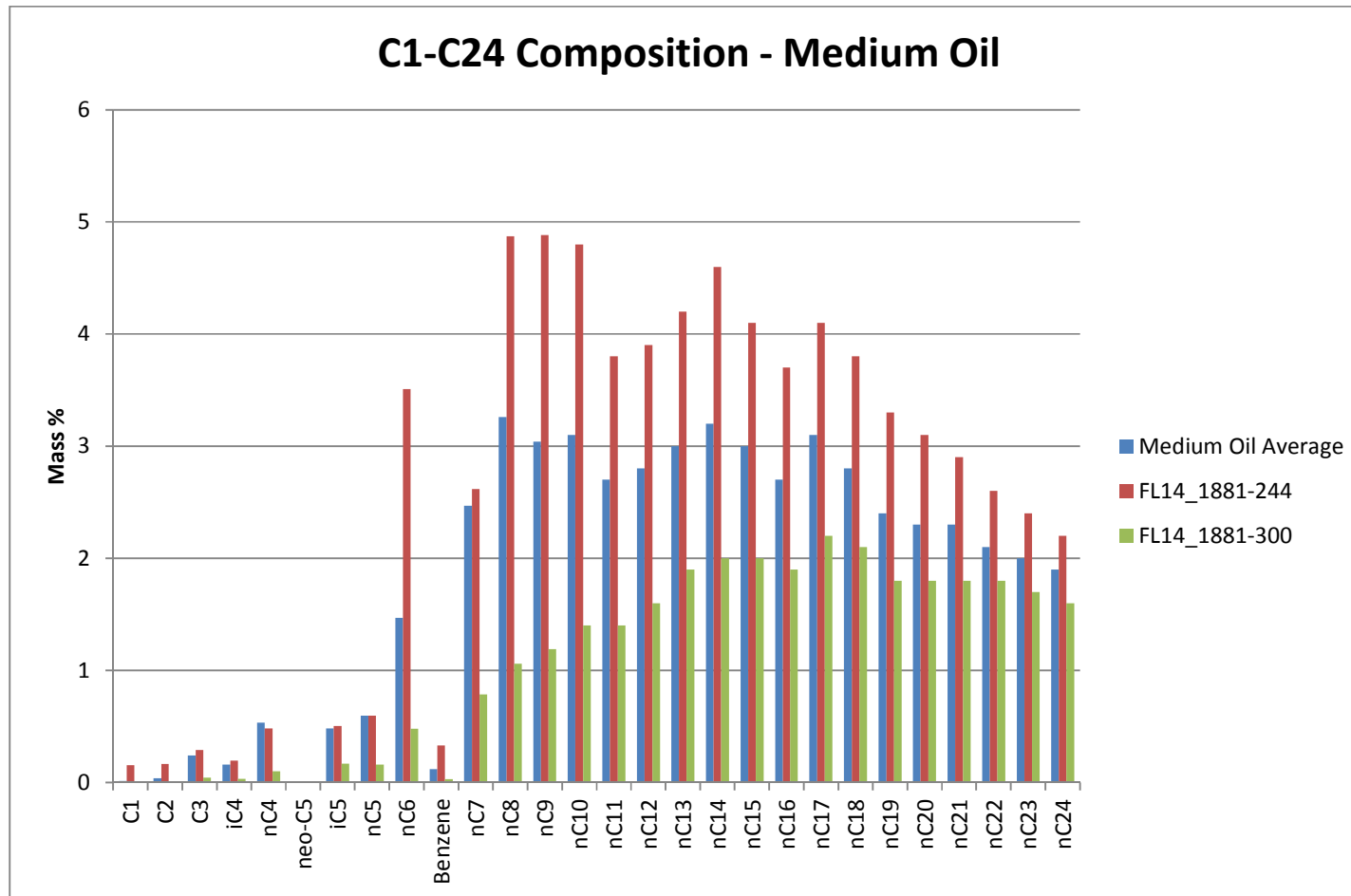


Figure 40: Medium Oil C1 to C24 Composition

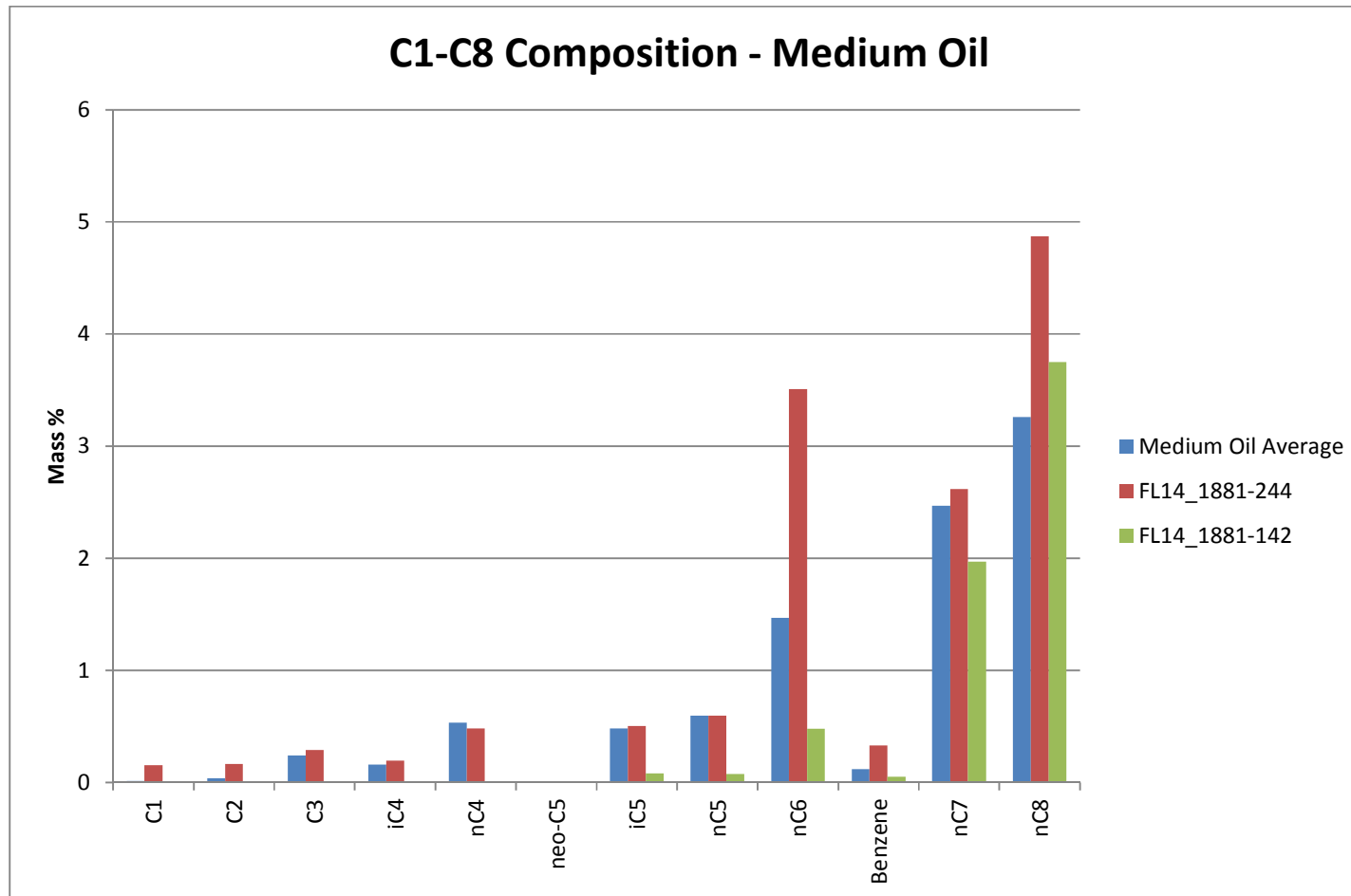


Figure 41: Medium Oil C1 to C8 Composition



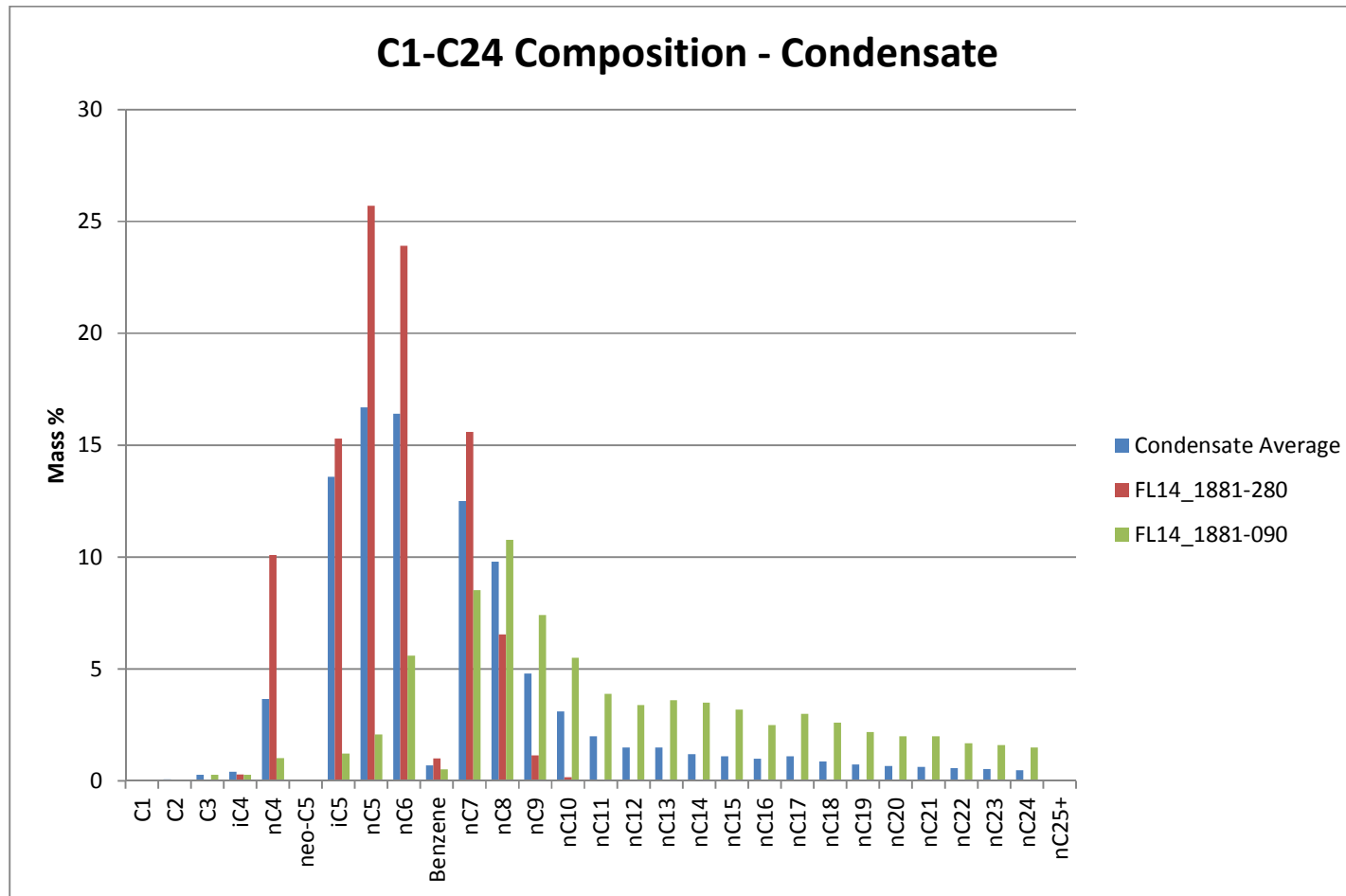


Figure 42: Condensate C1 to C24 Composition

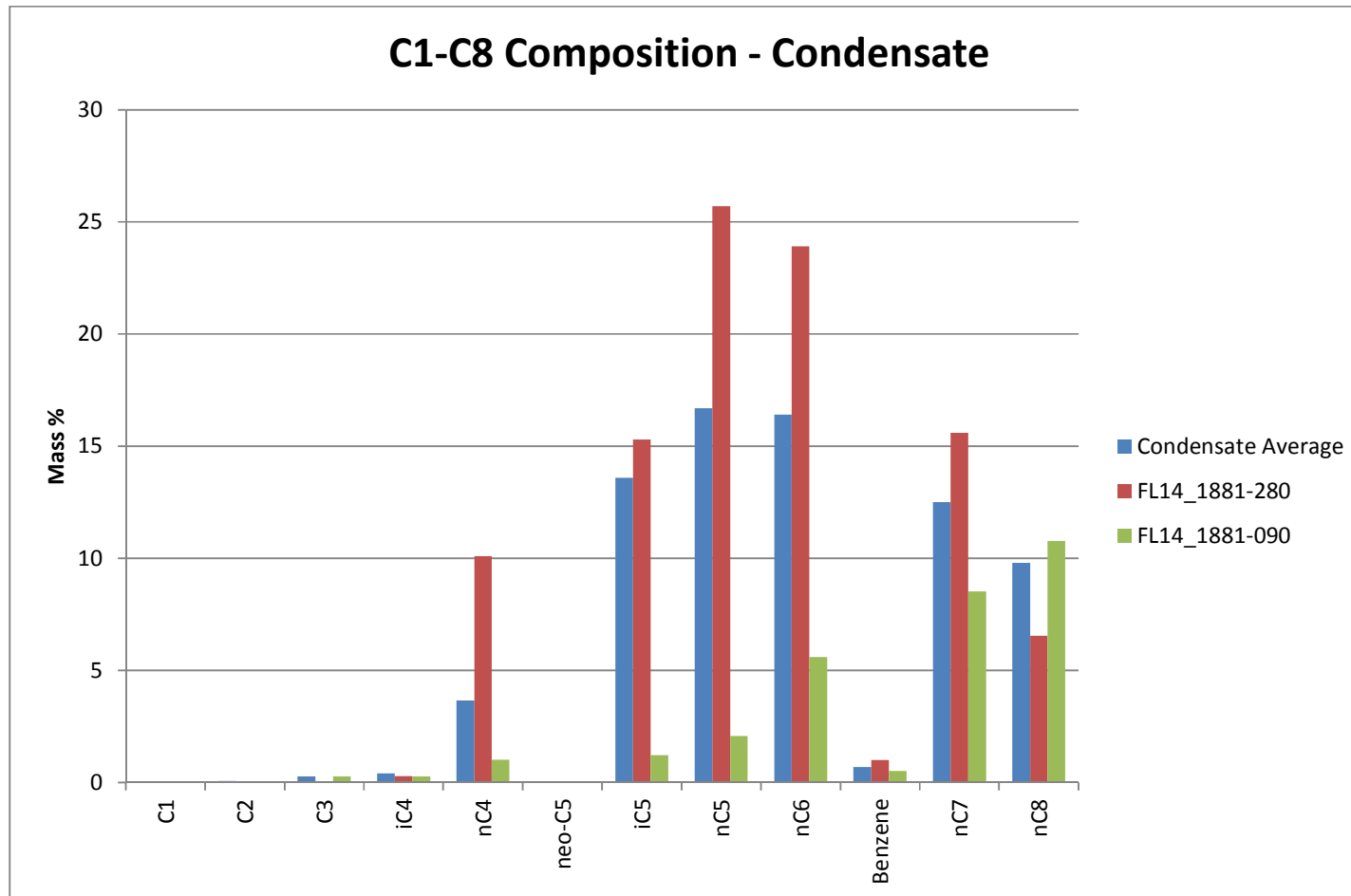


Figure 43: Condensate C1 to C8 Composition

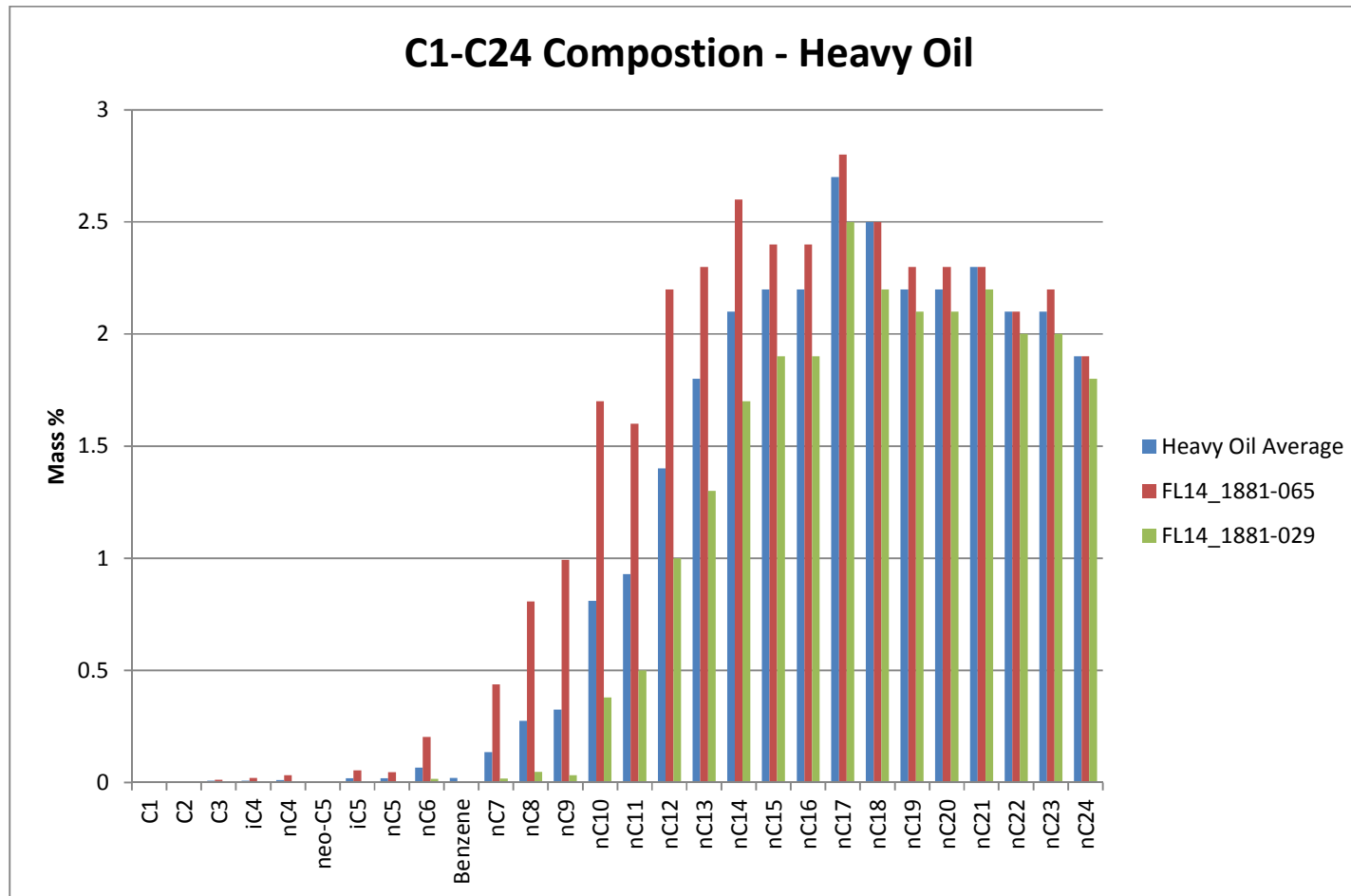


Figure 44: Heavy Oil C1 to C24 Composition

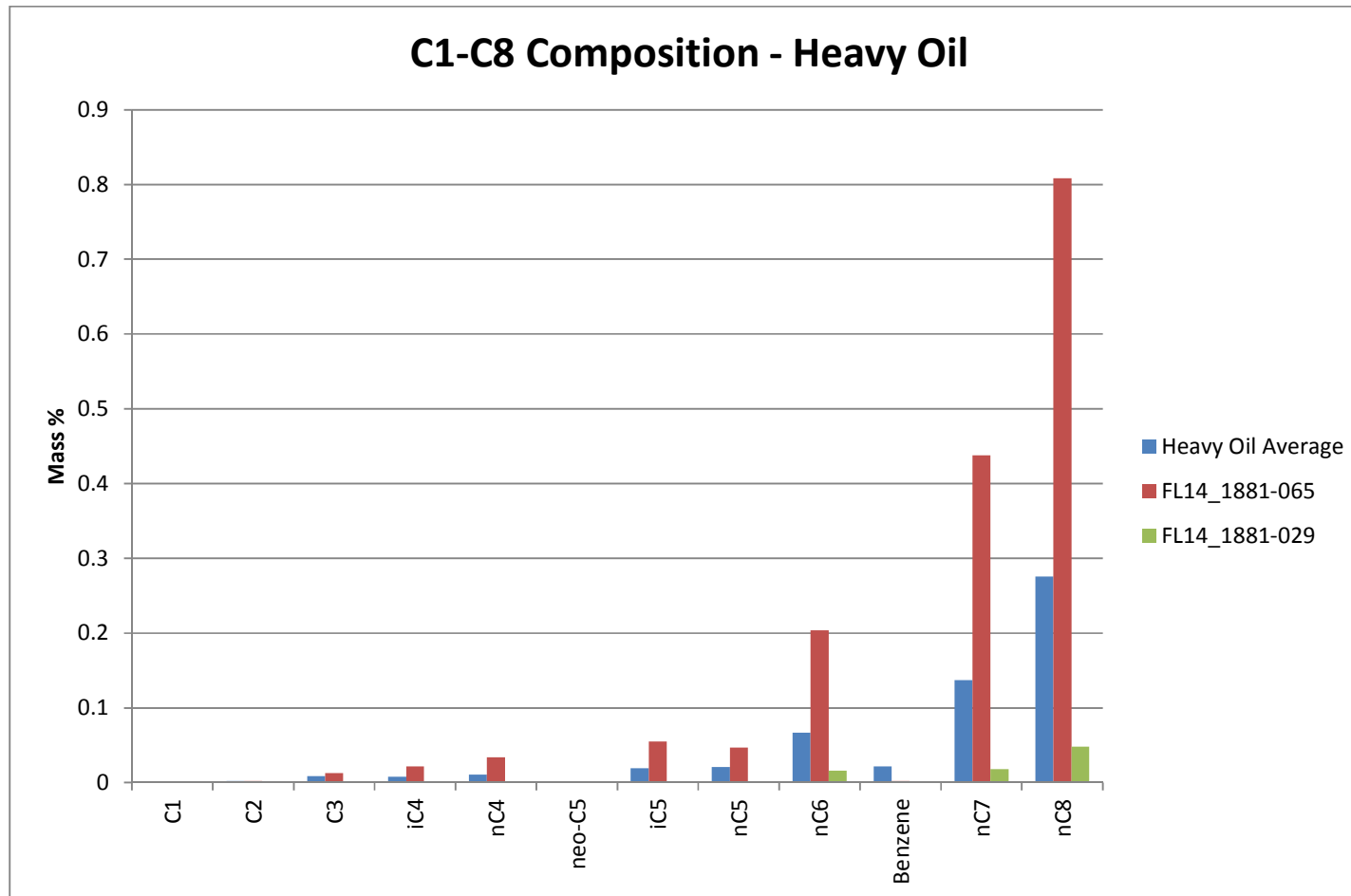


Figure 45: Heavy Oil C1 to C8 Composition

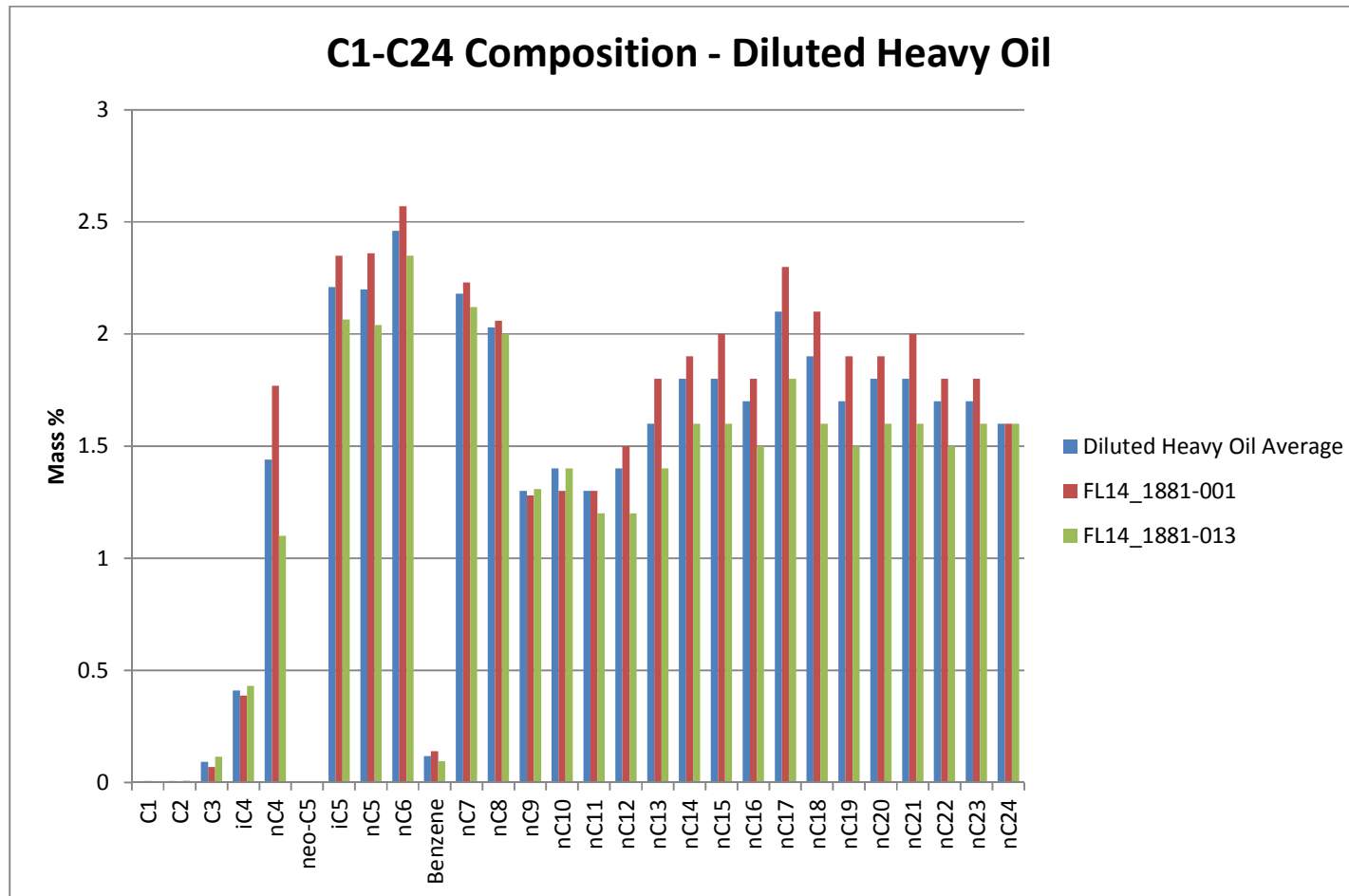


Figure 46: Diluted Heavy Oil C1 to C24 Composition

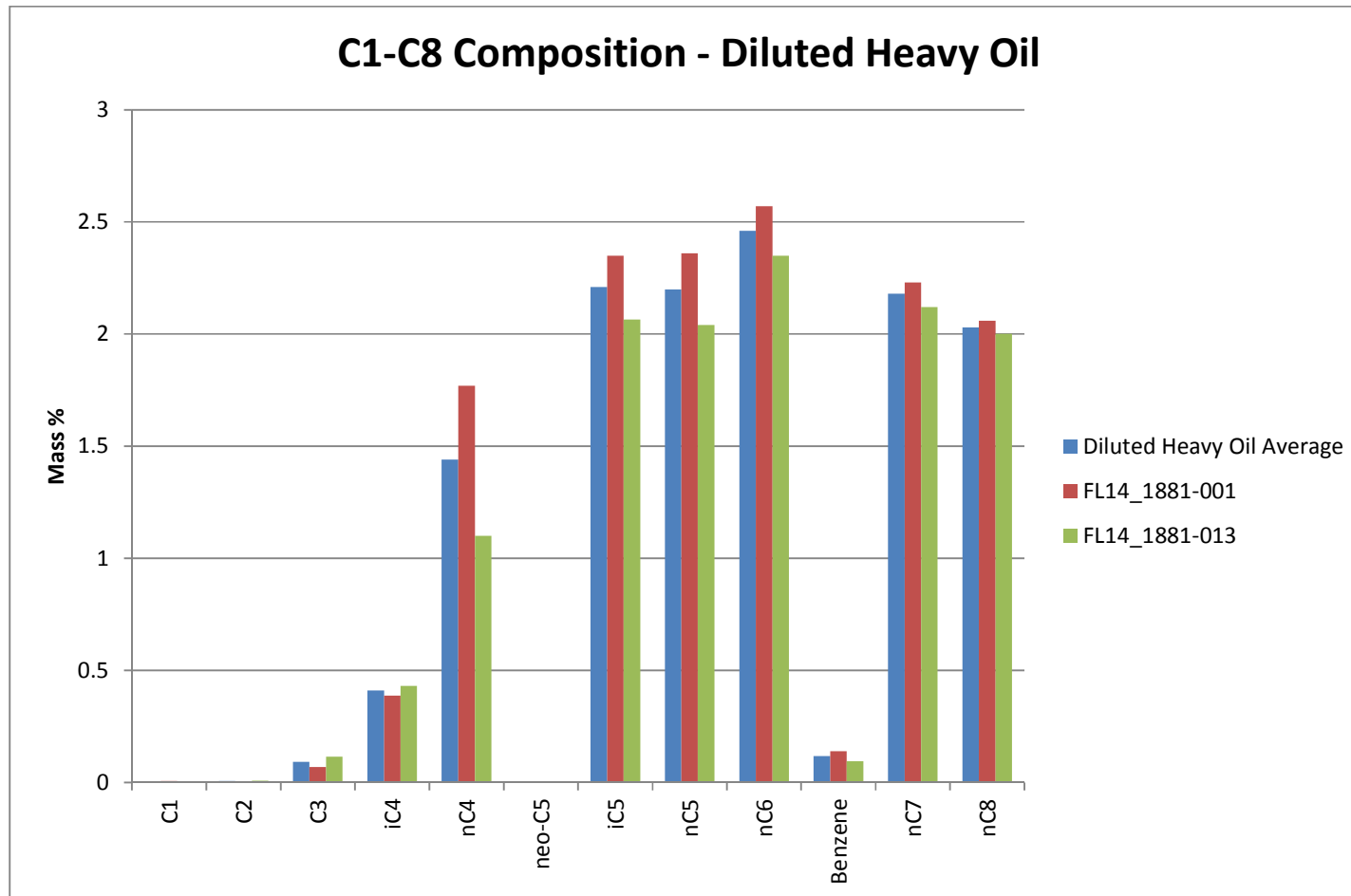


Figure 47: Diluted Heavy Oil C1 to C8 Composition

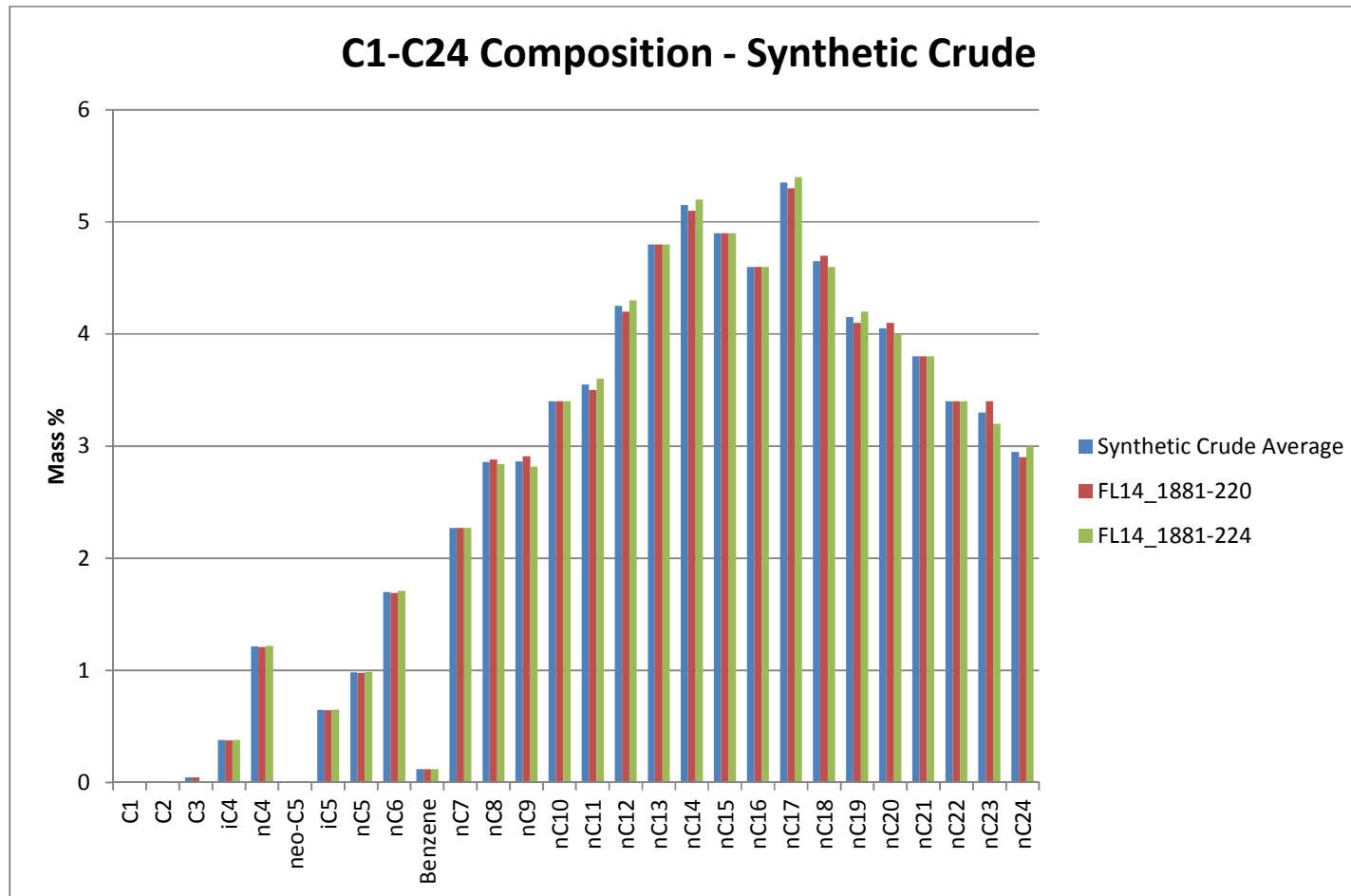


Figure 48: Synthetic Crude C1 to C24 Composition

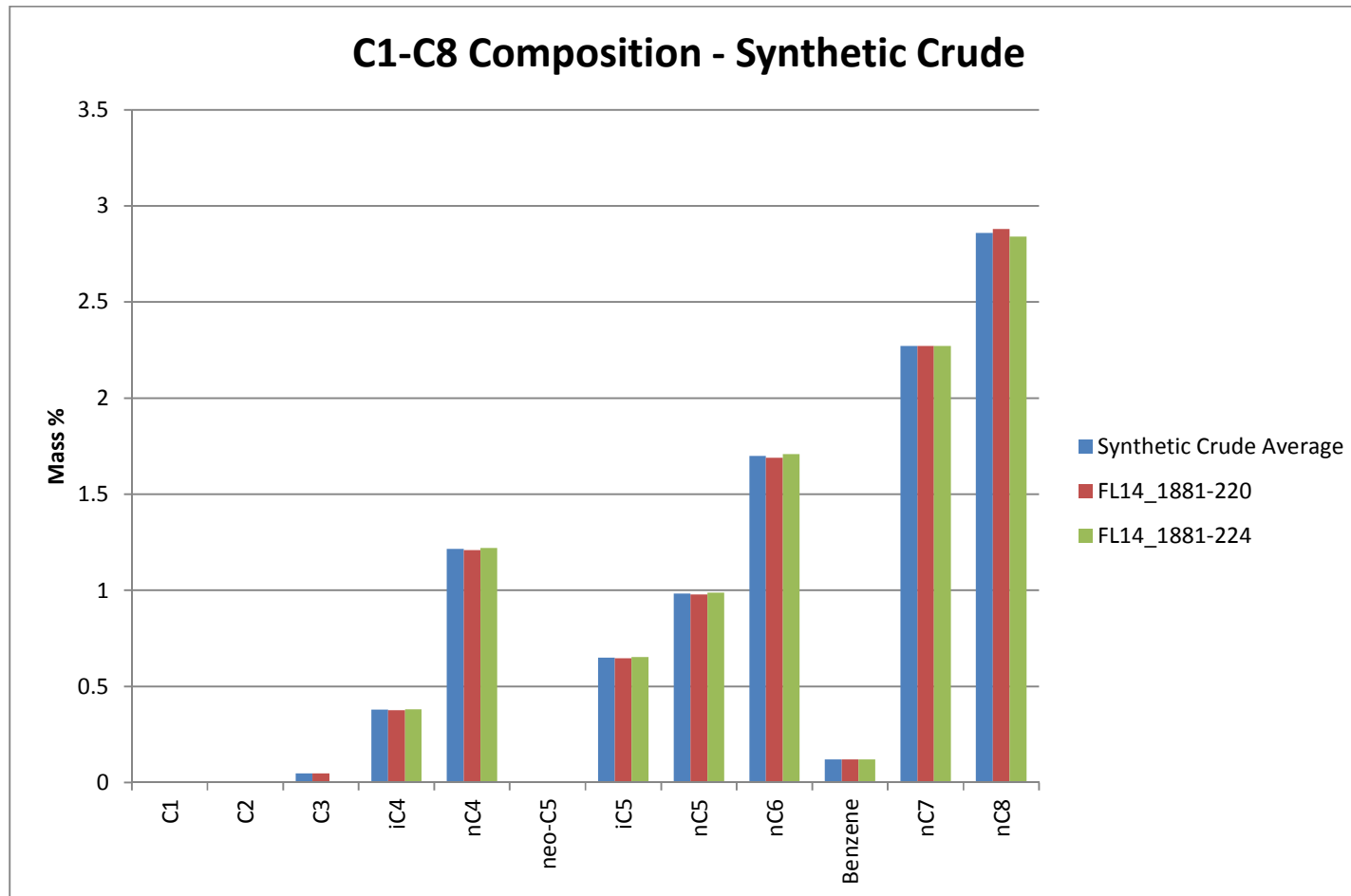


Figure 49: Synthetic Crude C1 to C8 Composition



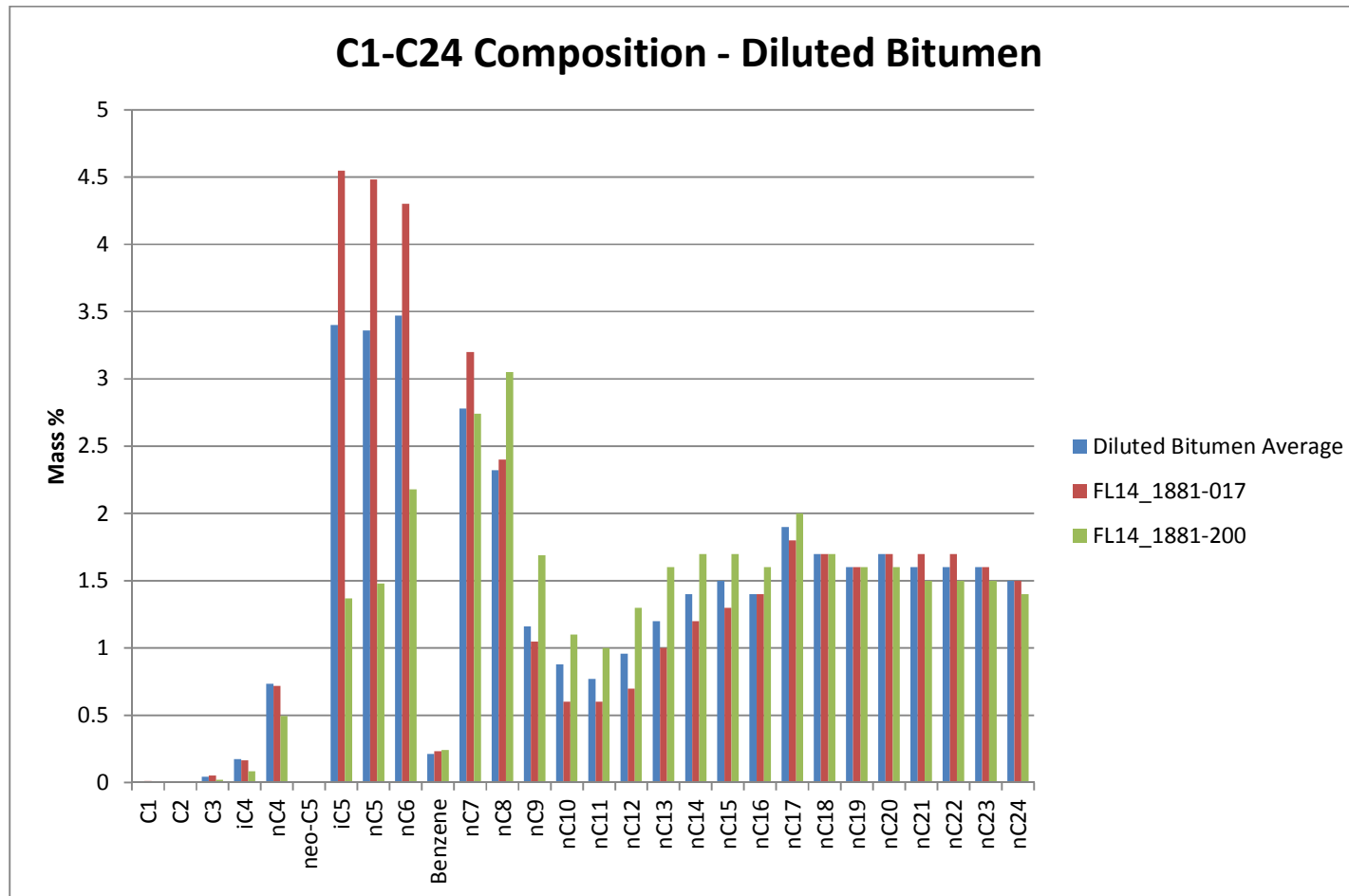


Figure 50: Dilbit C1 to C24 Composition

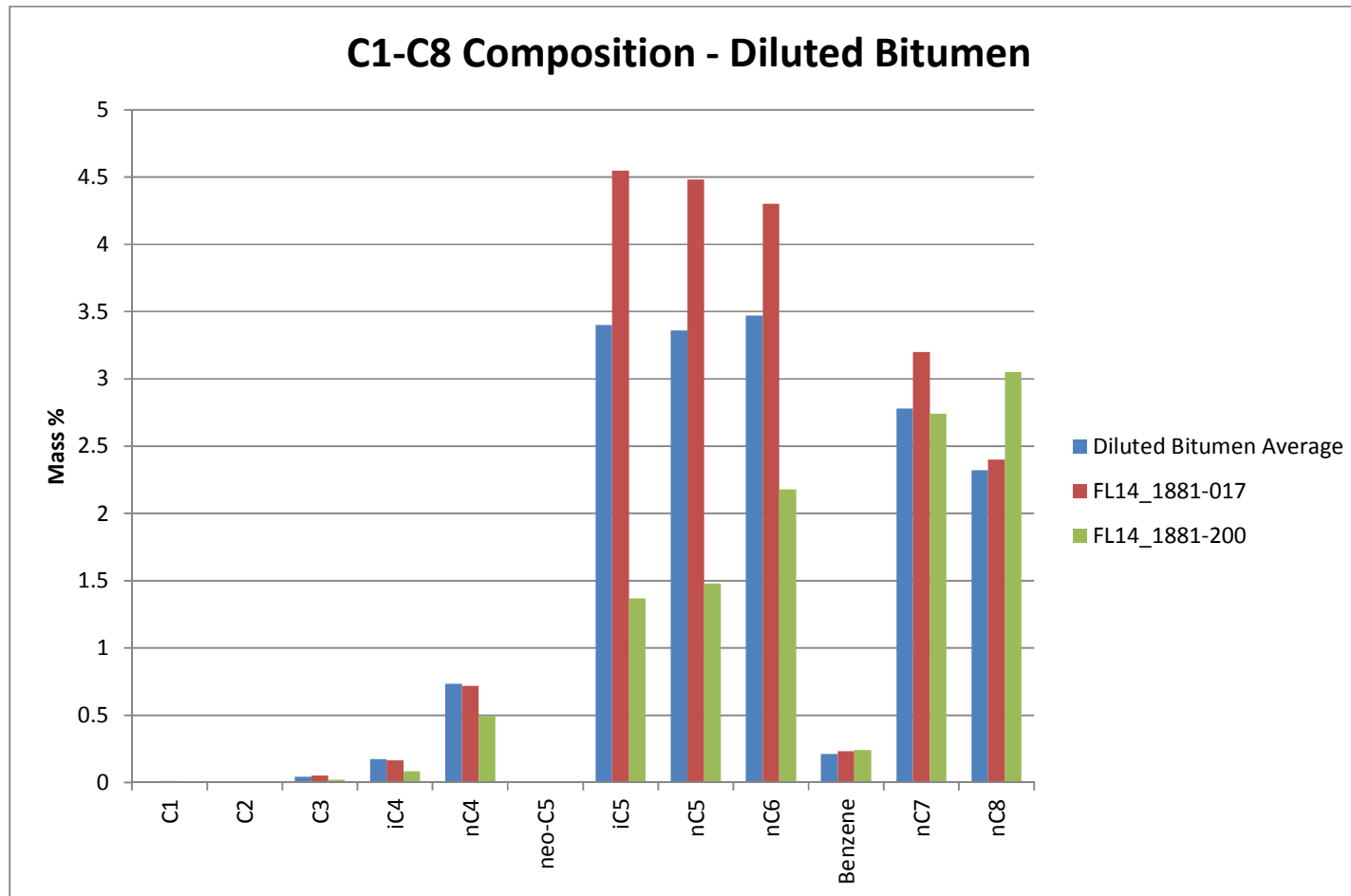


Figure 51: Dilbit C1 to C8 Composition

The ASTM D8003 and ASTM D7169 chromatograms of an example synthetic bitumen, light oil, medium oil, synthetic crude, dilbit, diluted synthetic bitumen and condensate are shown in Figures 52 to 67. In each ASTM D8003 chromatogram, the section from C1 to C6 has been magnified to demonstrate the clear separation of the light ends.

In the ASTM D7169 chromatograms, the incomplete separation of peaks in the C4 to C8 region can be seen. These chromatograms are shown with the CS<sub>2</sub> blank run subtracted. The section between C1 to C6 has been magnified for sample FL14\_1881-232 (synthetic bitumen) without and with the CS<sub>2</sub> subtracted, Figures 54 and 55 respectively, to demonstrate the effect of the large amount of carbon disulphide solvent.

# ANNEX B - AITF REPORT (EN)

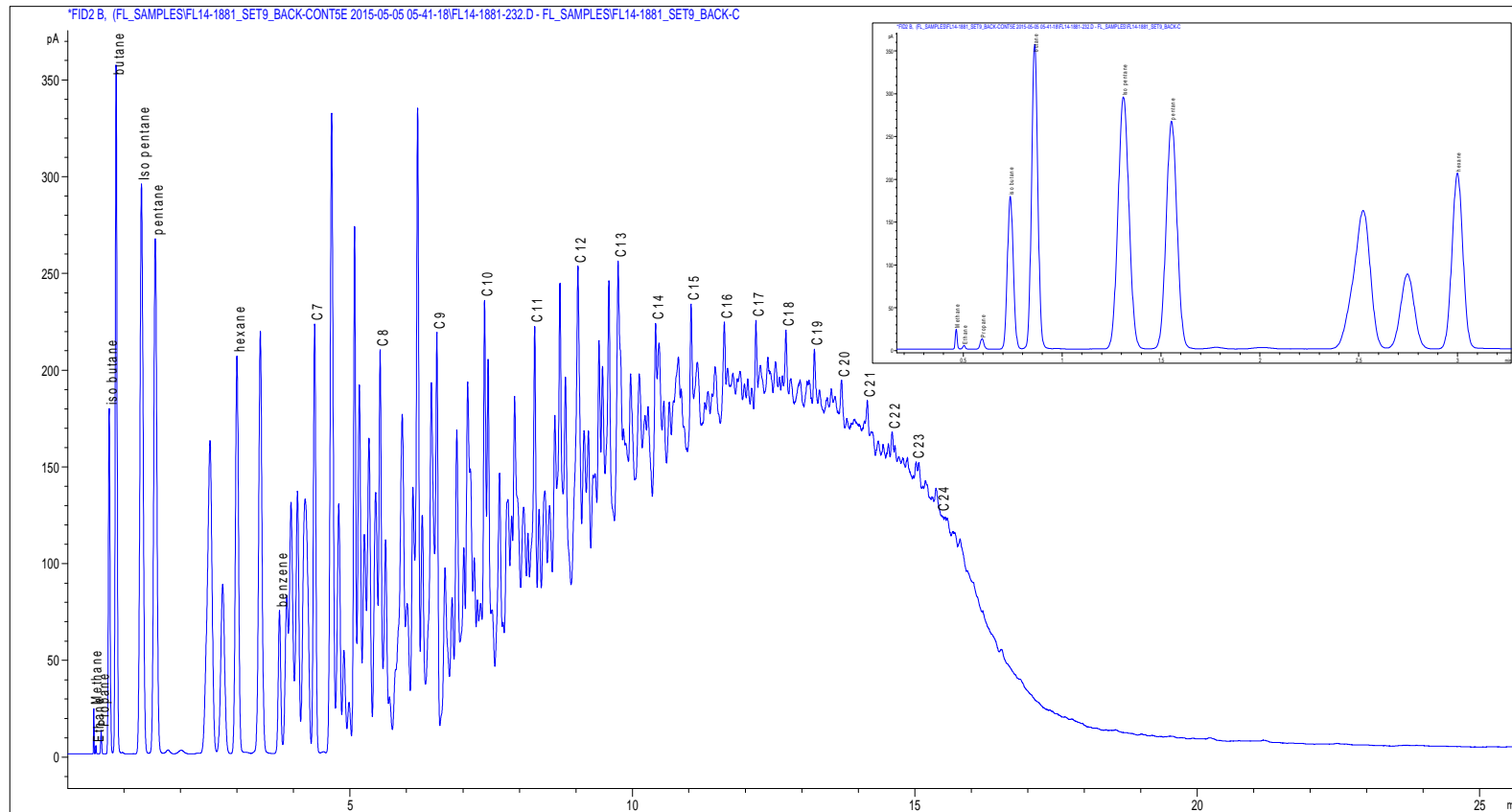


Figure 52: ASTM D8003 Chromatogram of a Synthetic Bitumen, FL14\_1881-232

# ANNEX B - AITF REPORT (EN)

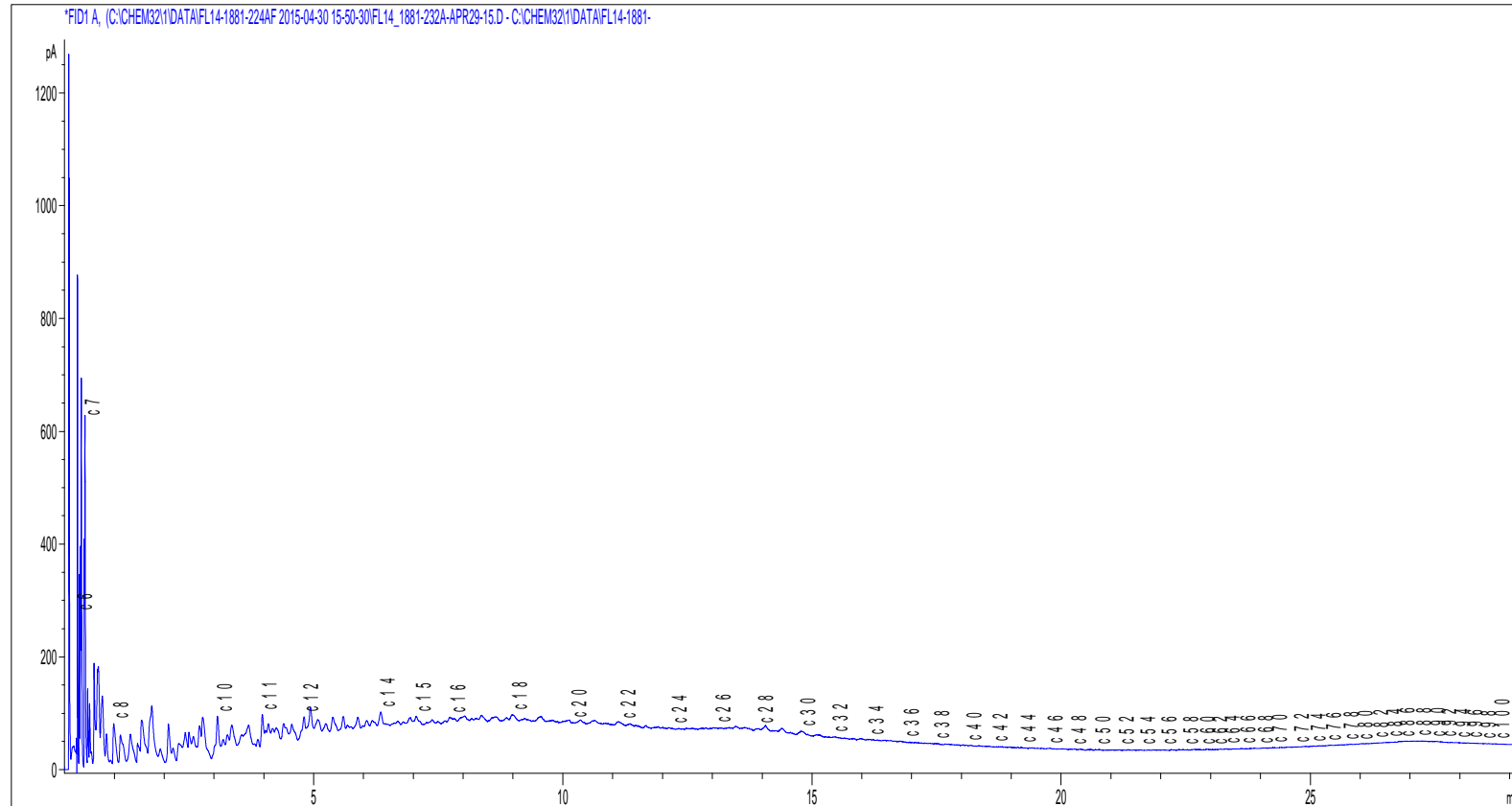


Figure 53: ASTM D7169 Chromatogram of a Synthetic Bitumen, FL14\_1881-232

# ANNEX B - AITF REPORT (EN)

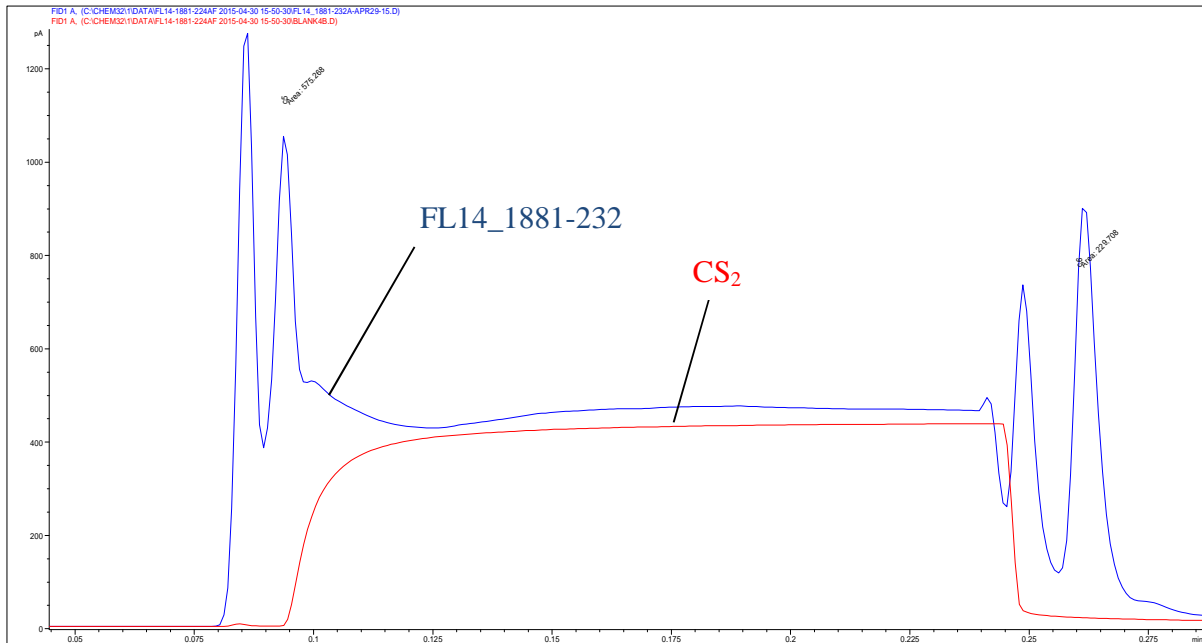


Figure 54: ASTM D7169 (C1 to C6) Chromatogram of a Synthetic Bitumen, FL14\_1881-232; CS<sub>2</sub> not subtracted

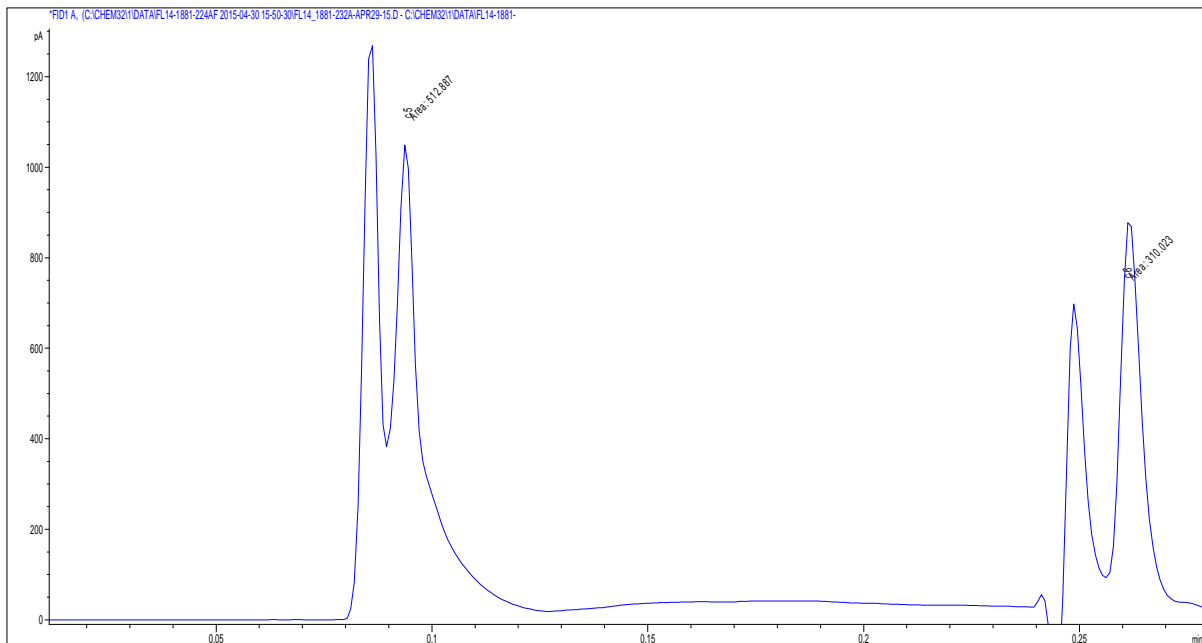


Figure 55: ASTM D7169 (C1 to C6) Chromatogram of a Synthetic Bitumen, FL14\_1881-232; CS<sub>2</sub> subtracted

# ANNEX B - AITF REPORT (EN)

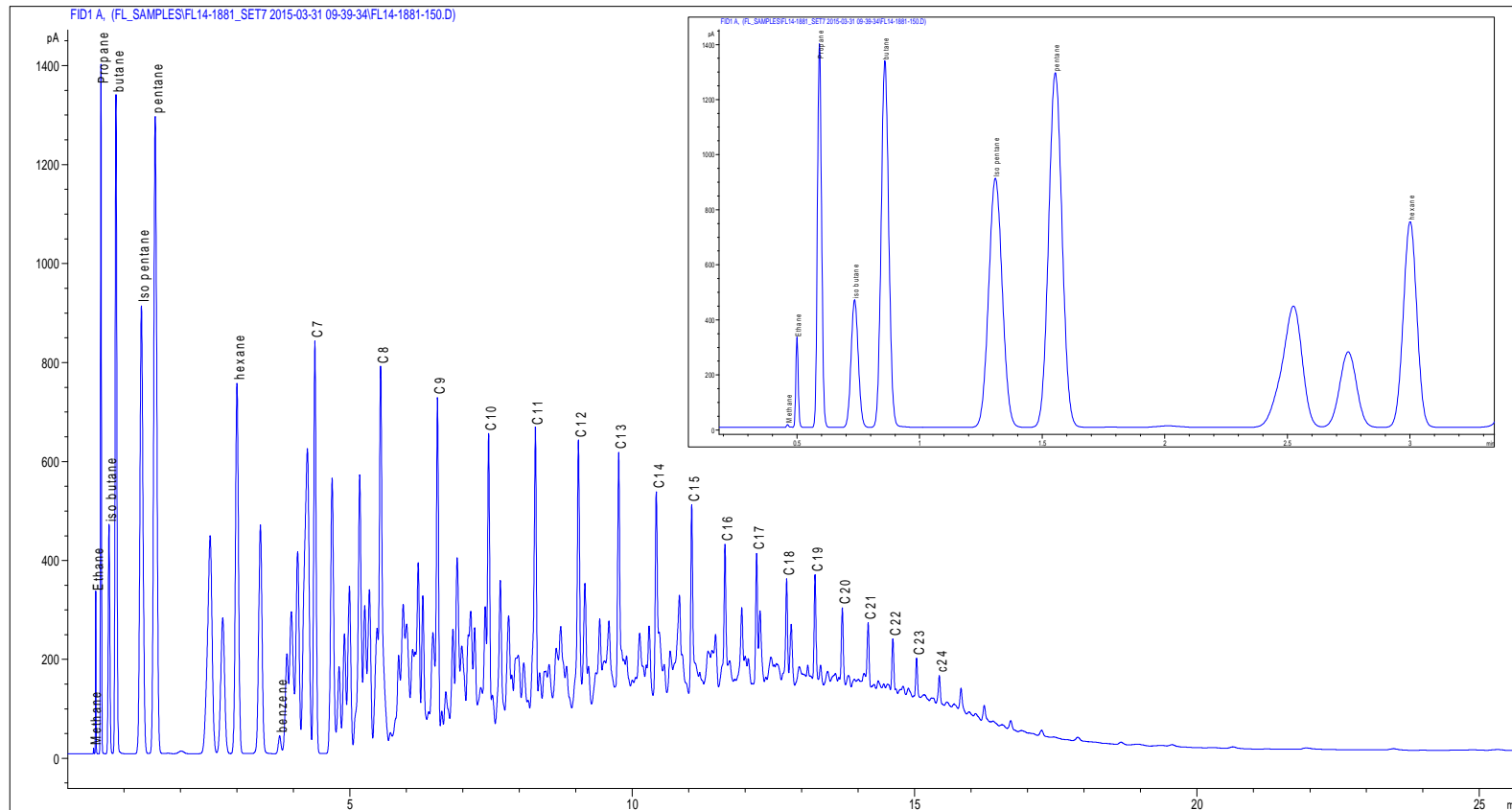


Figure 56: ASTM D8003 Chromatogram of a Light Oil, FL14-1881-150

# ANNEX B - AITF REPORT (EN)

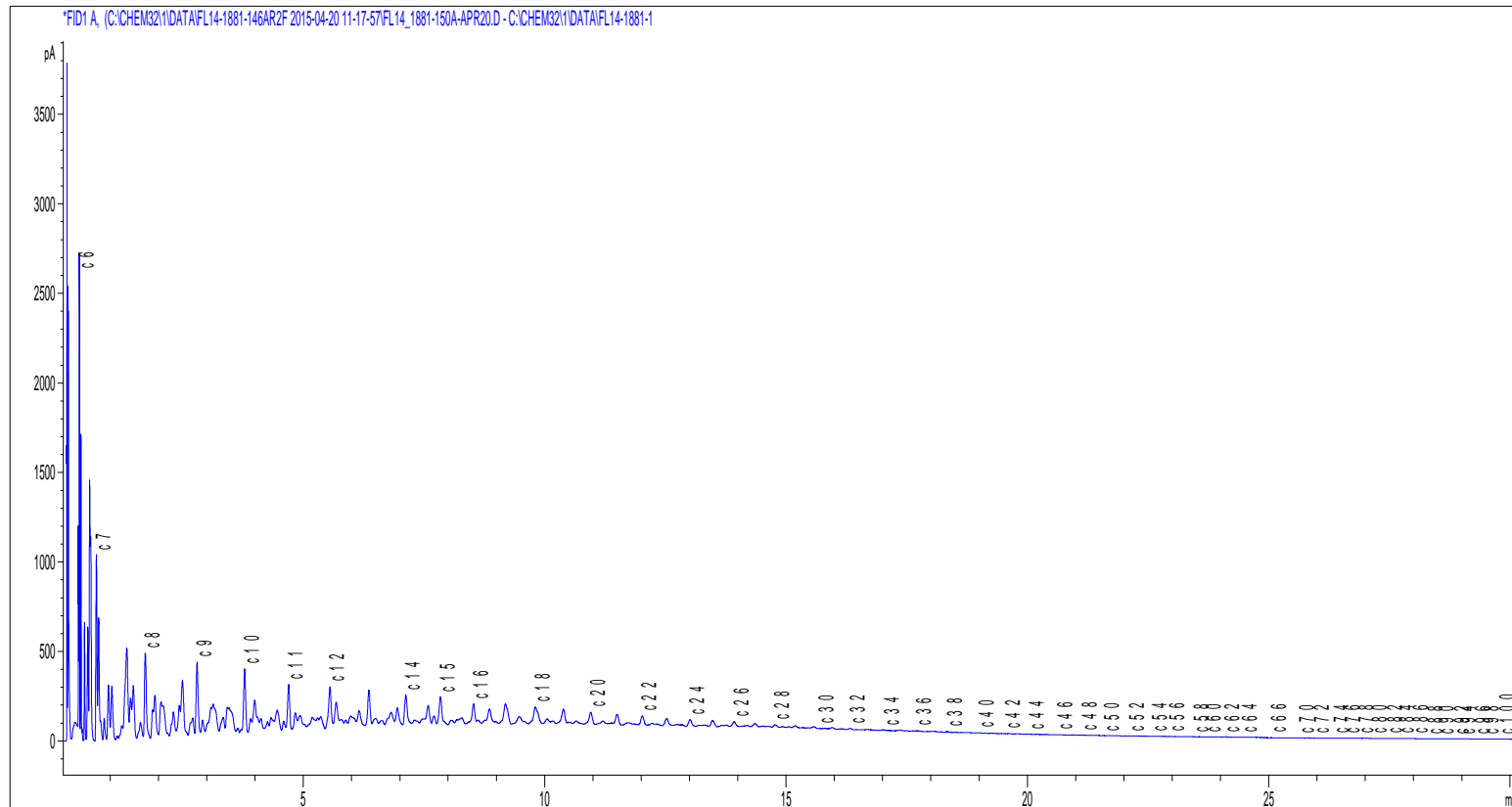


Figure 57: ASTM D7169 Chromatogram of a Light Oil, FL14-1881-150



# ANNEX B - AITF REPORT (EN)

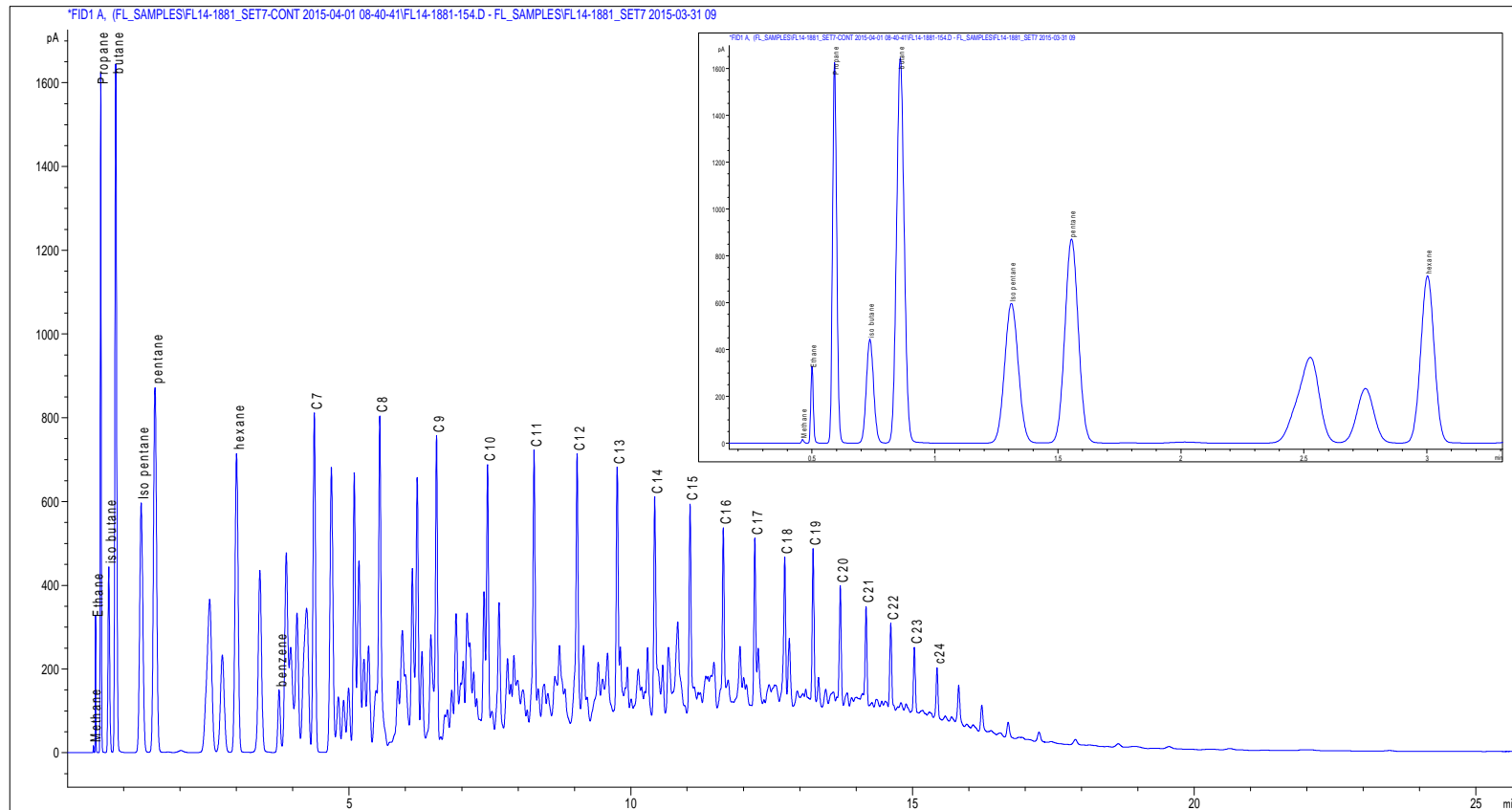


Figure 58: ASTM D8003 Chromatogram of a Medium Oil, FL14\_1881-154

# ANNEX B - AITF REPORT (EN)

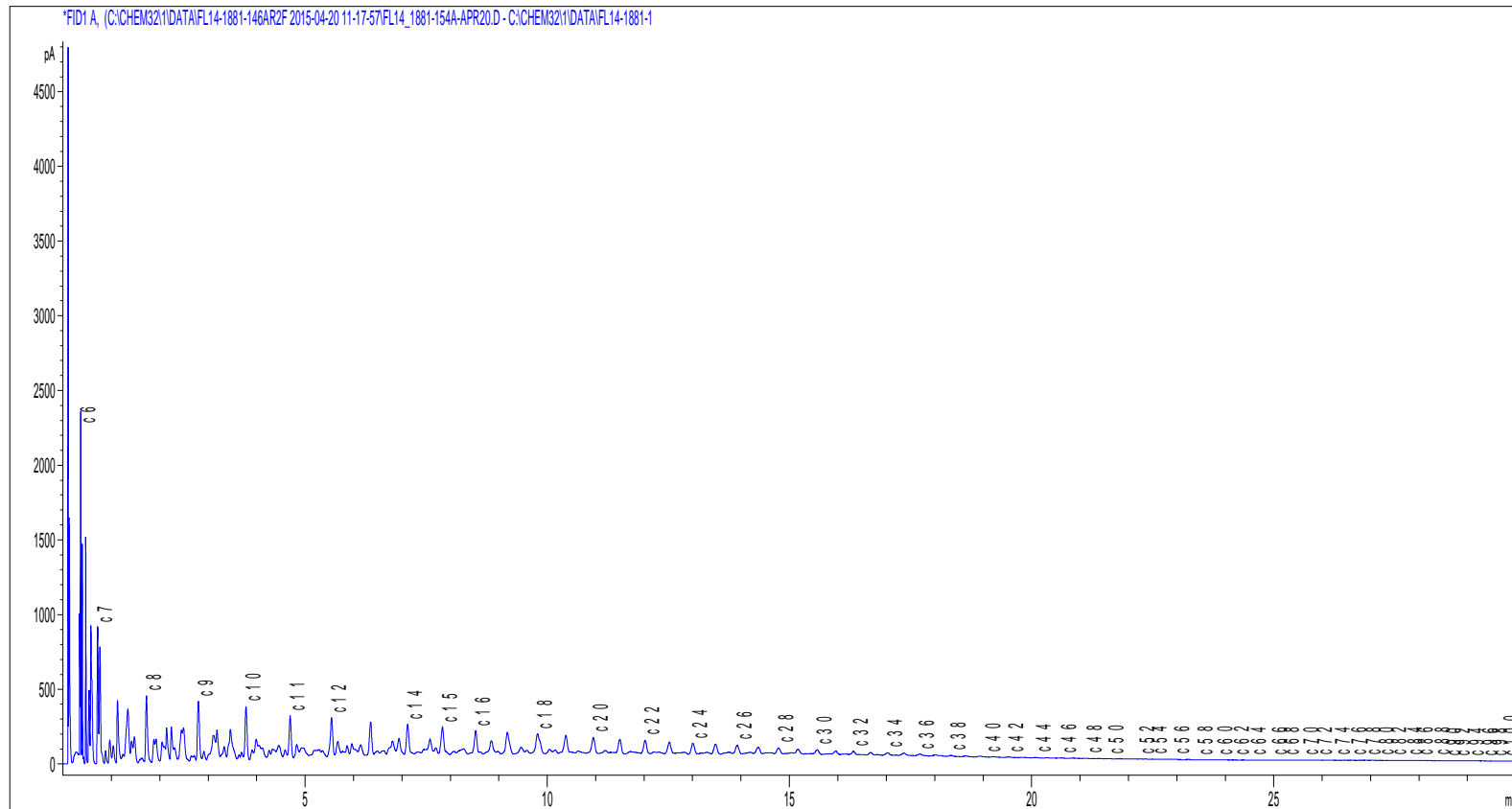


Figure 59: ASTM D7169 Chromatogram of a Medium Oil, FL14\_1881-154

# ANNEX B - AITF REPORT (EN)

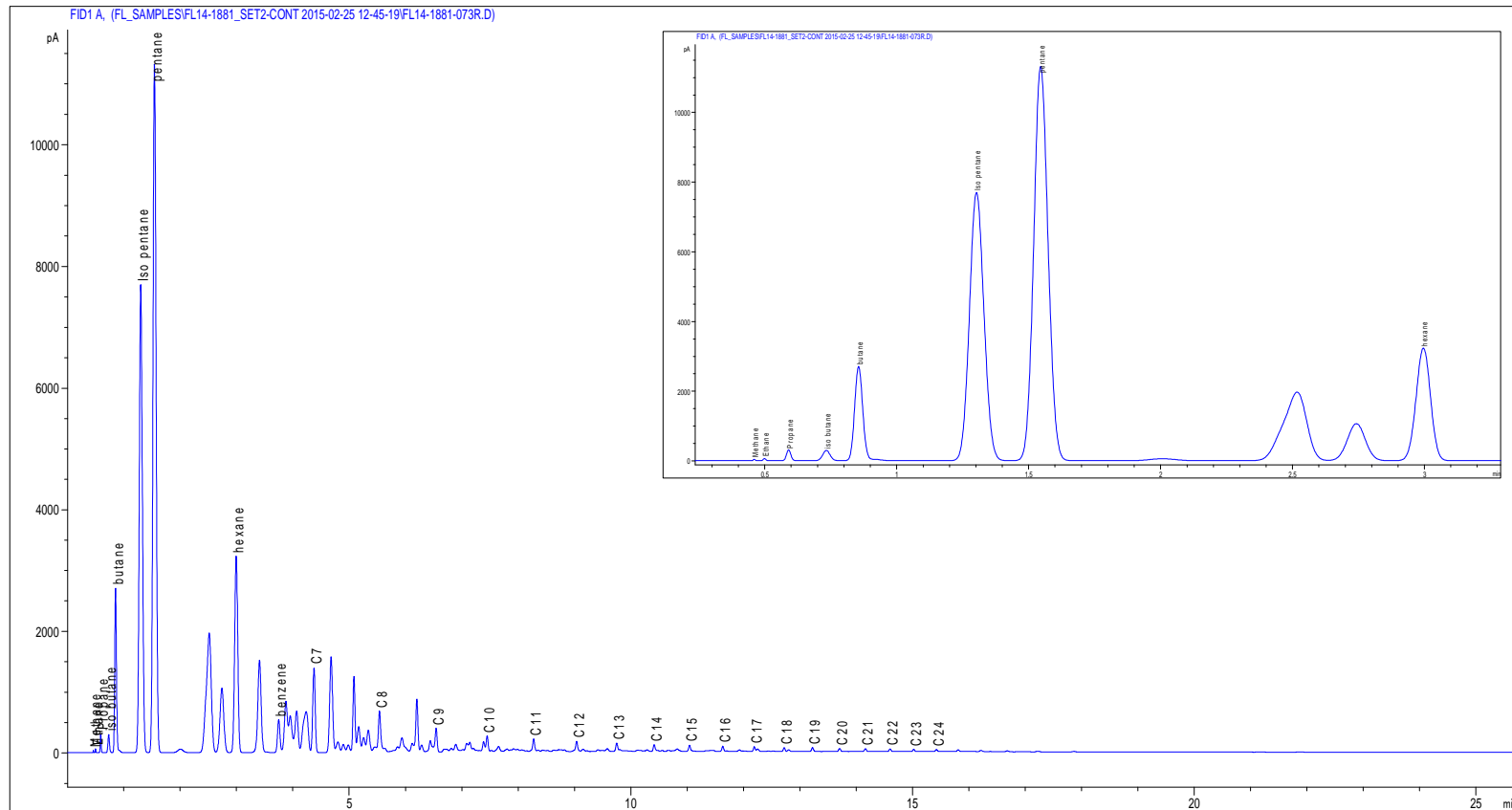


Figure 60: ASTM D8003 Chromatogram of a Condensate, FL14\_1881-073

# ANNEX B - AITF REPORT (EN)

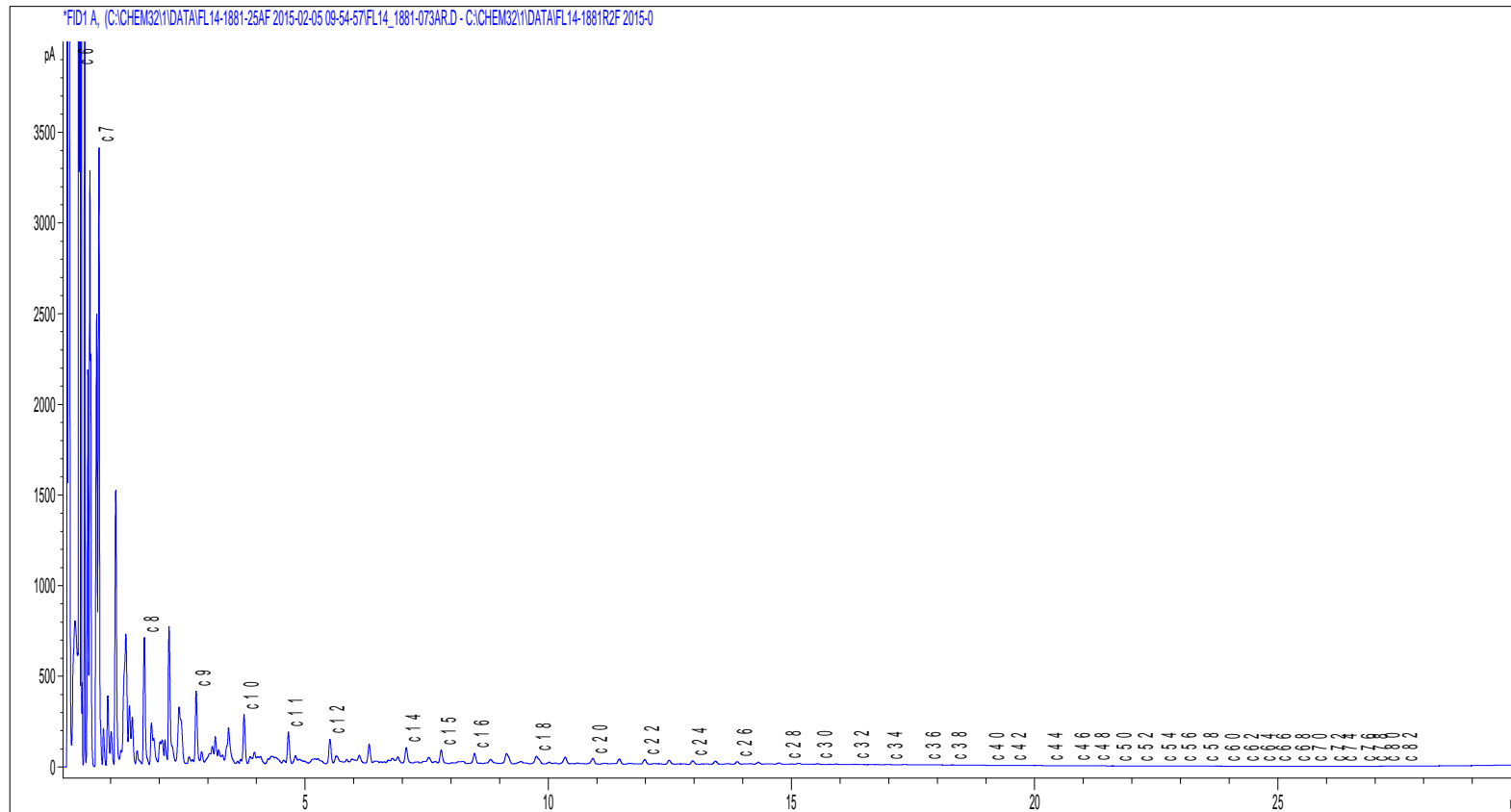


Figure 61: ASTM D7169 Chromatogram of a Condensate, FL14\_1881-073

# ANNEX B - AITF REPORT (EN)

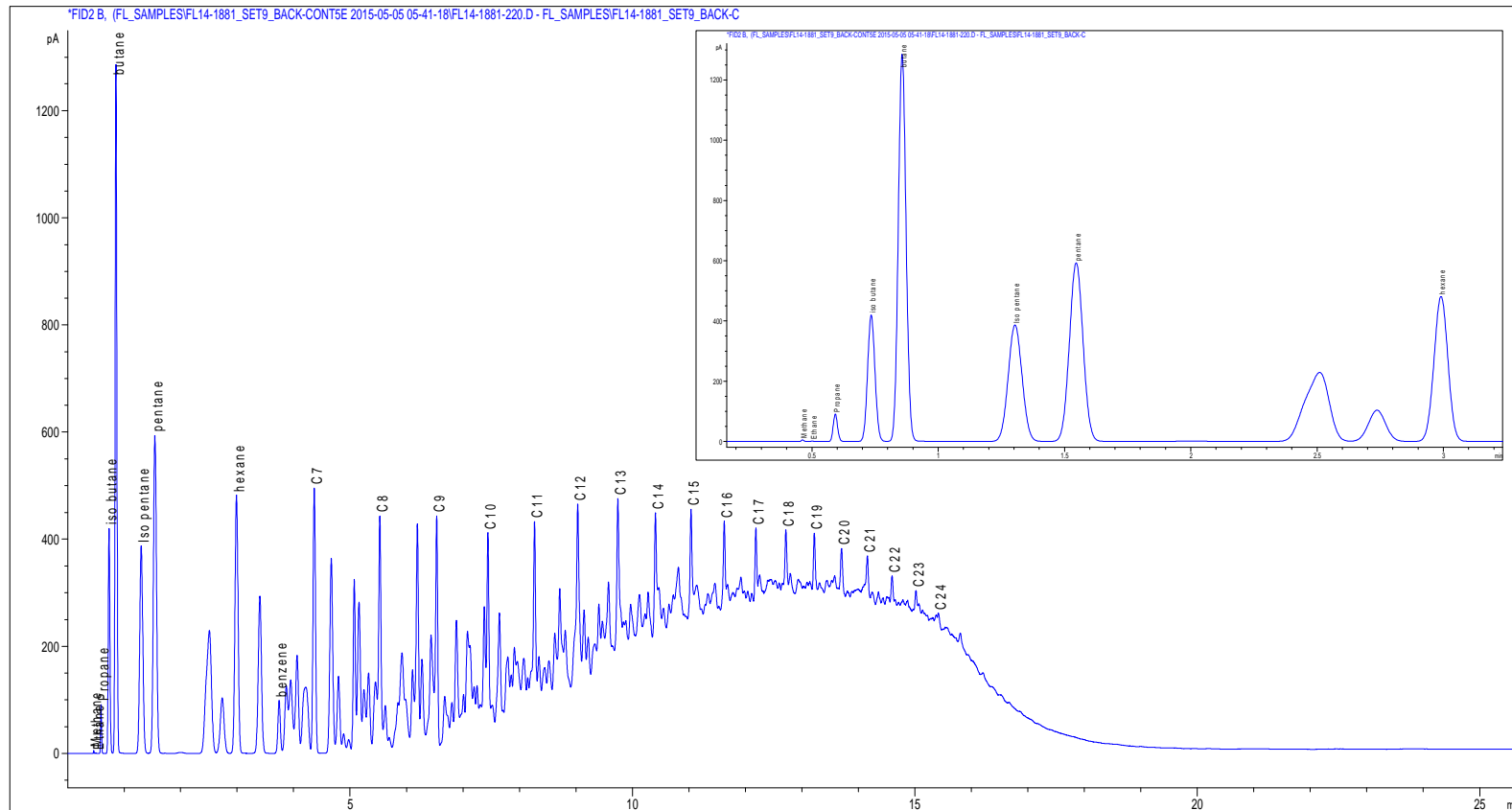


Figure 62: ASTM D8003 Chromatogram of a Synthetic Crude, FL14\_1881-220

# ANNEX B - AITF REPORT (EN)

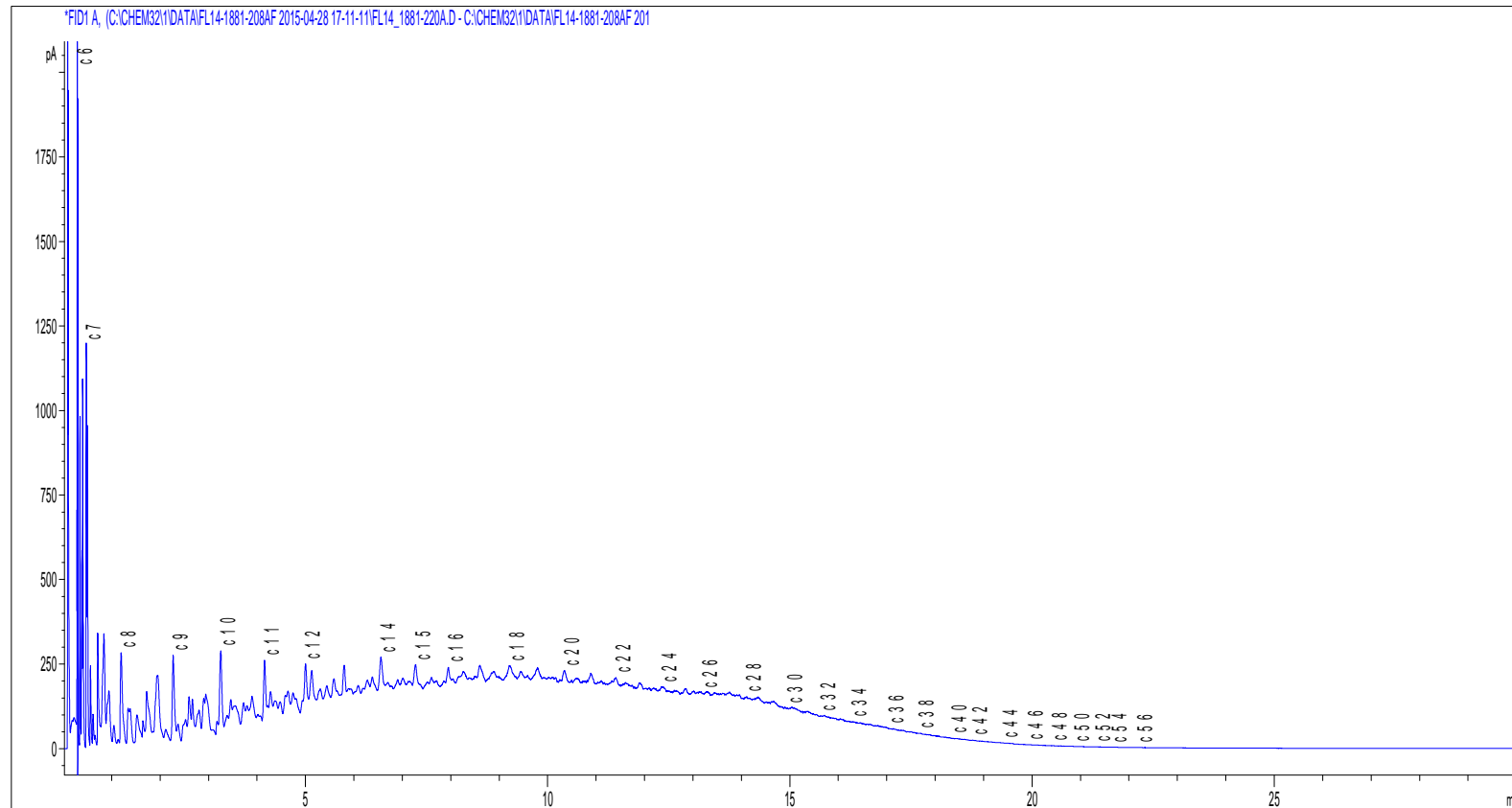


Figure 63: ASTM D7169 Chromatogram of a Synthetic Crude, FL14\_1881-220

# ANNEX B - AITF REPORT (EN)

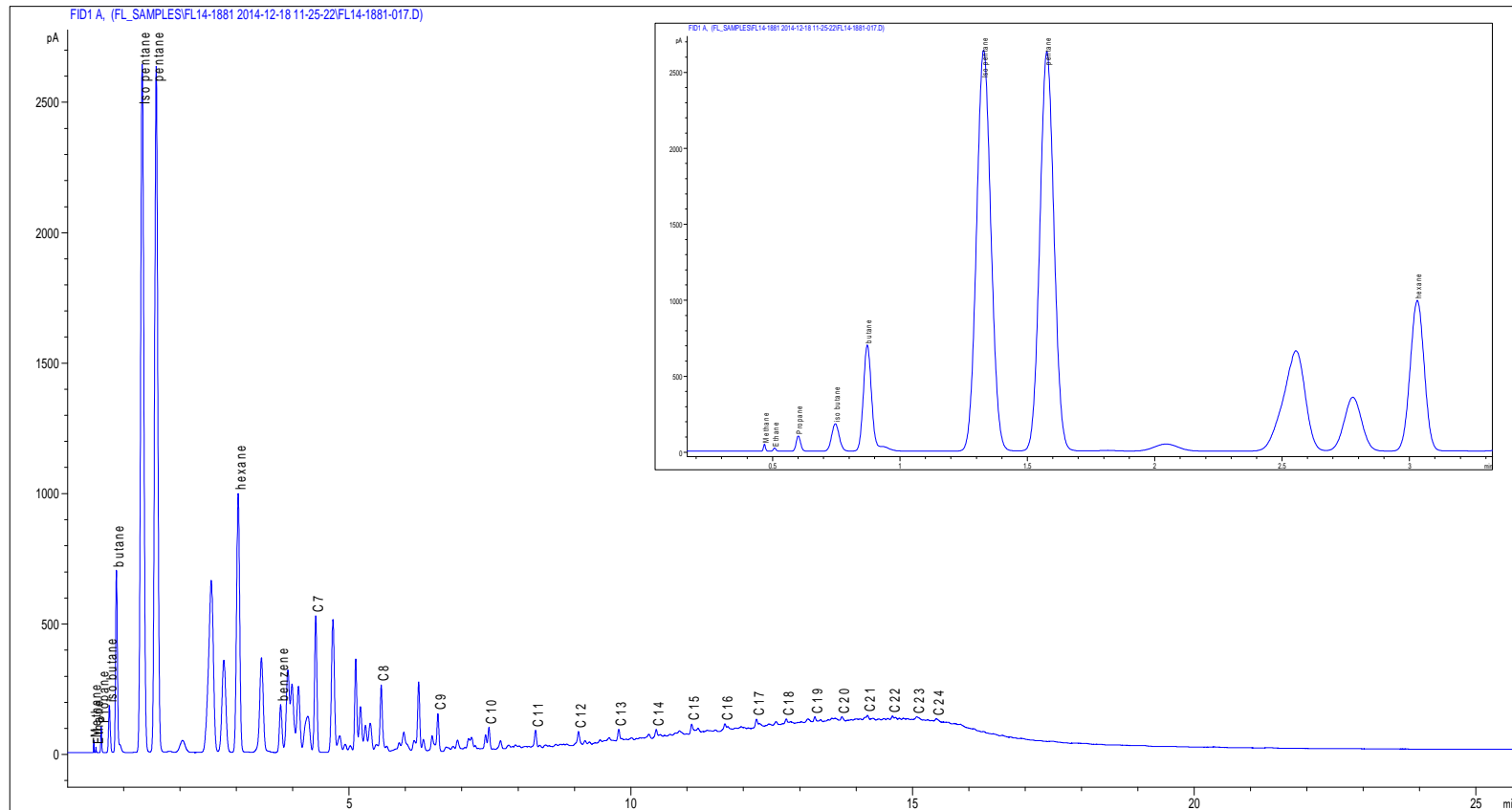


Figure 64: ASTM D8003 Chromatogram of a Dilbit, FL14\_1881-017

# ANNEX B - AITF REPORT (EN)

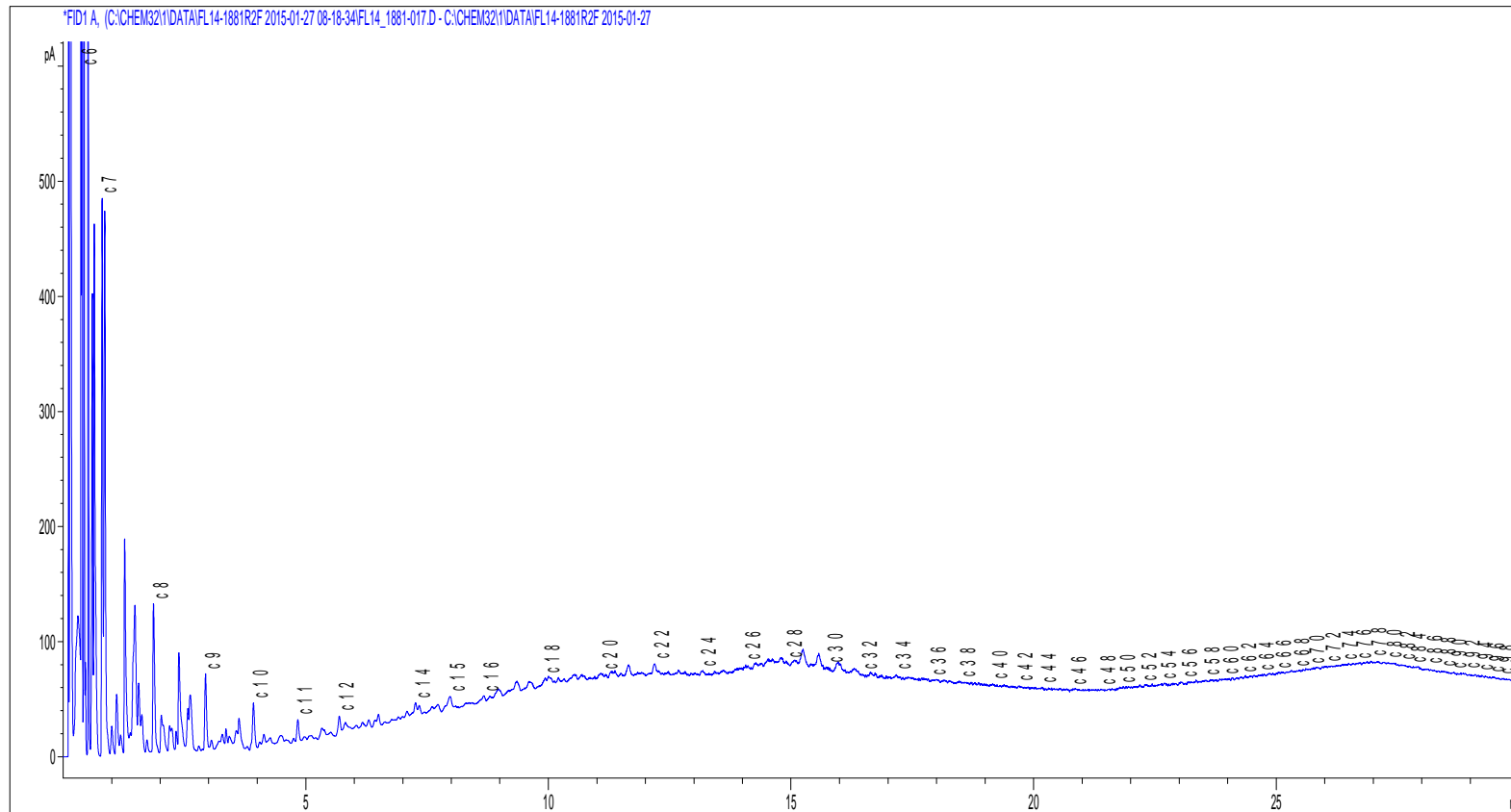


Figure 65: ASTM D7169 Chromatogram of a Dilbit, FL14\_1881-017



# ANNEX B - AITF REPORT (EN)

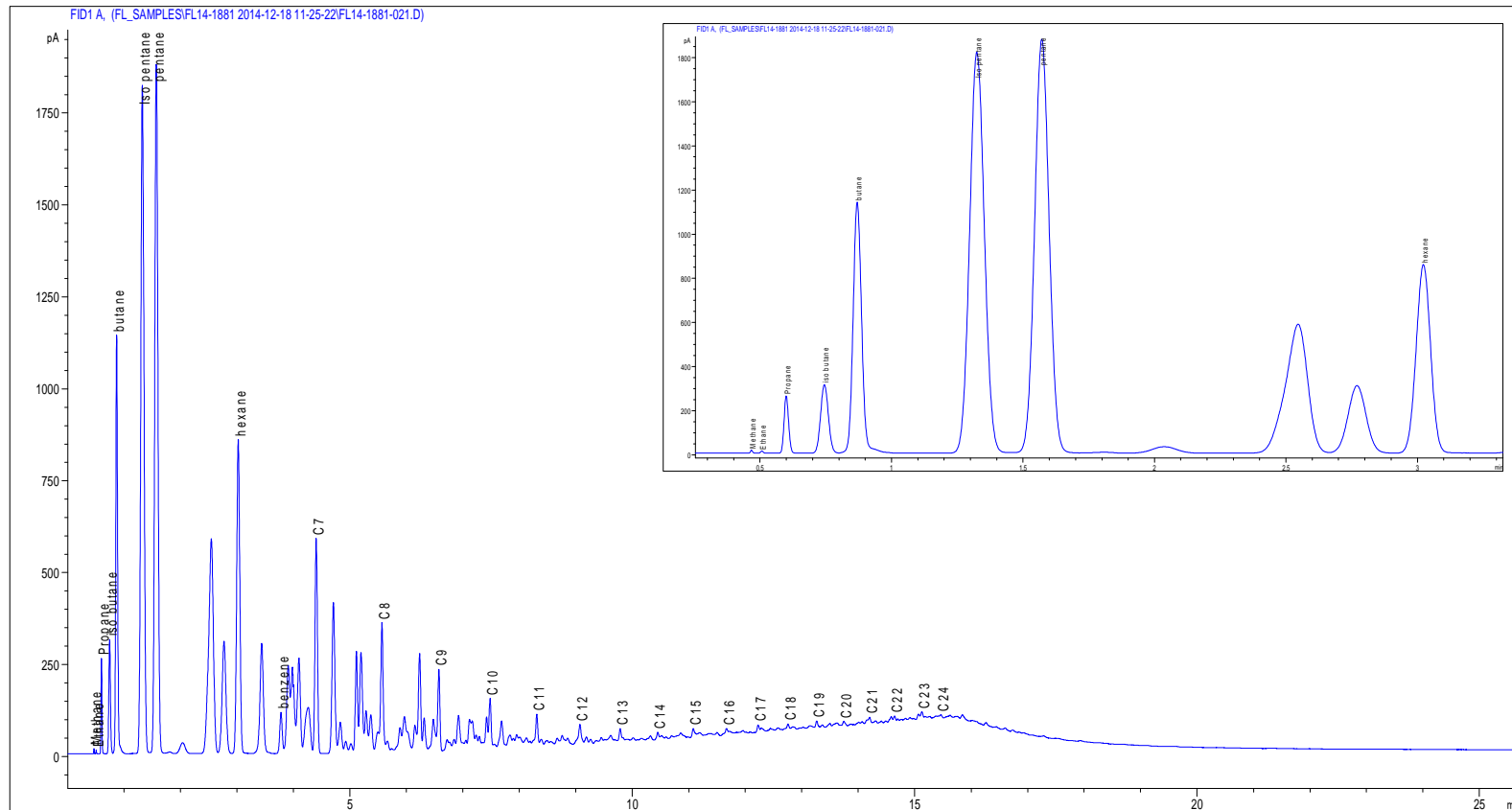


Figure 66: ASTM D8003 Chromatogram of a Diluted Synthetic Bitumen, FL14\_1881-021

# ANNEX B - AITF REPORT (EN)

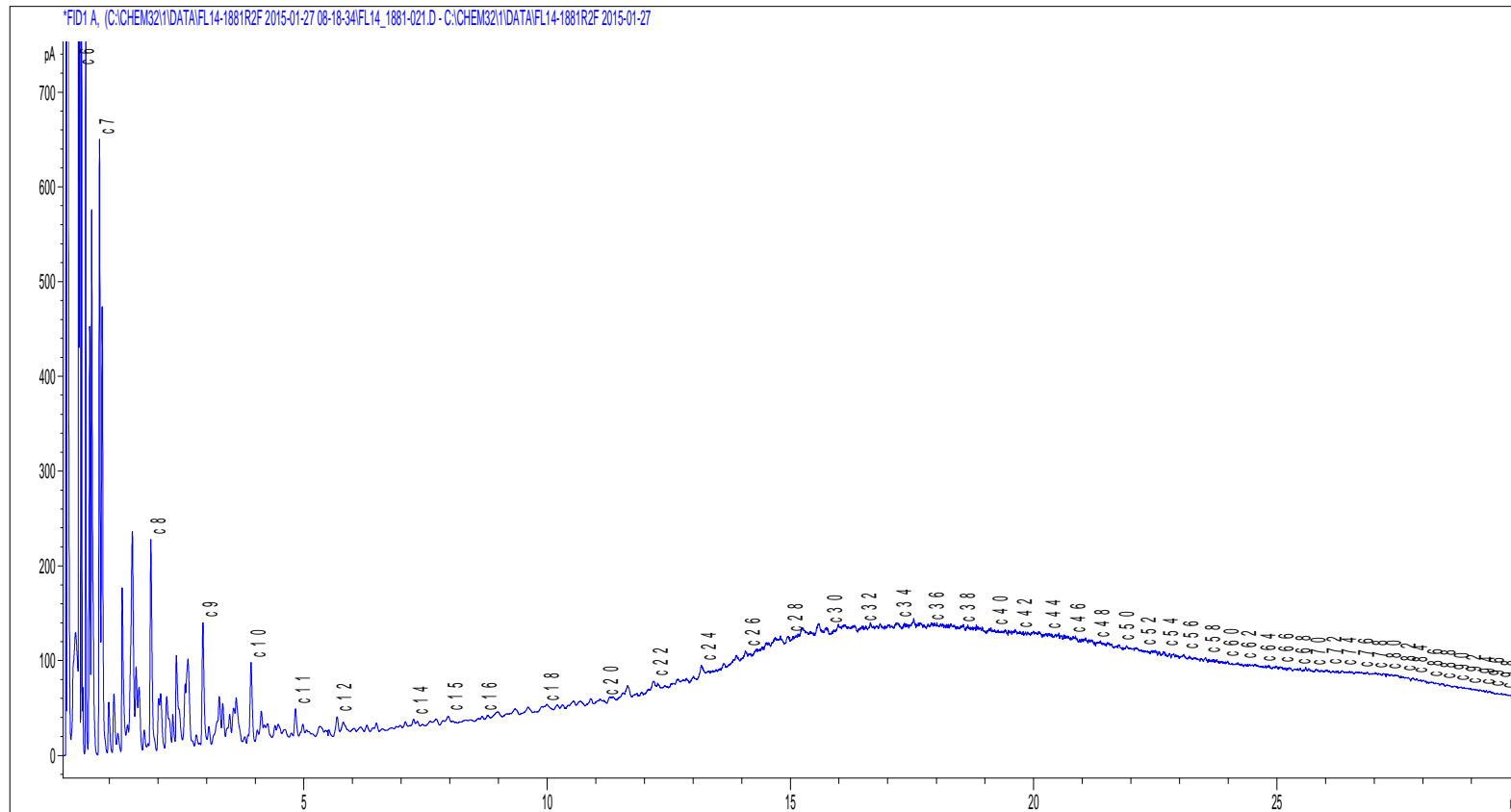
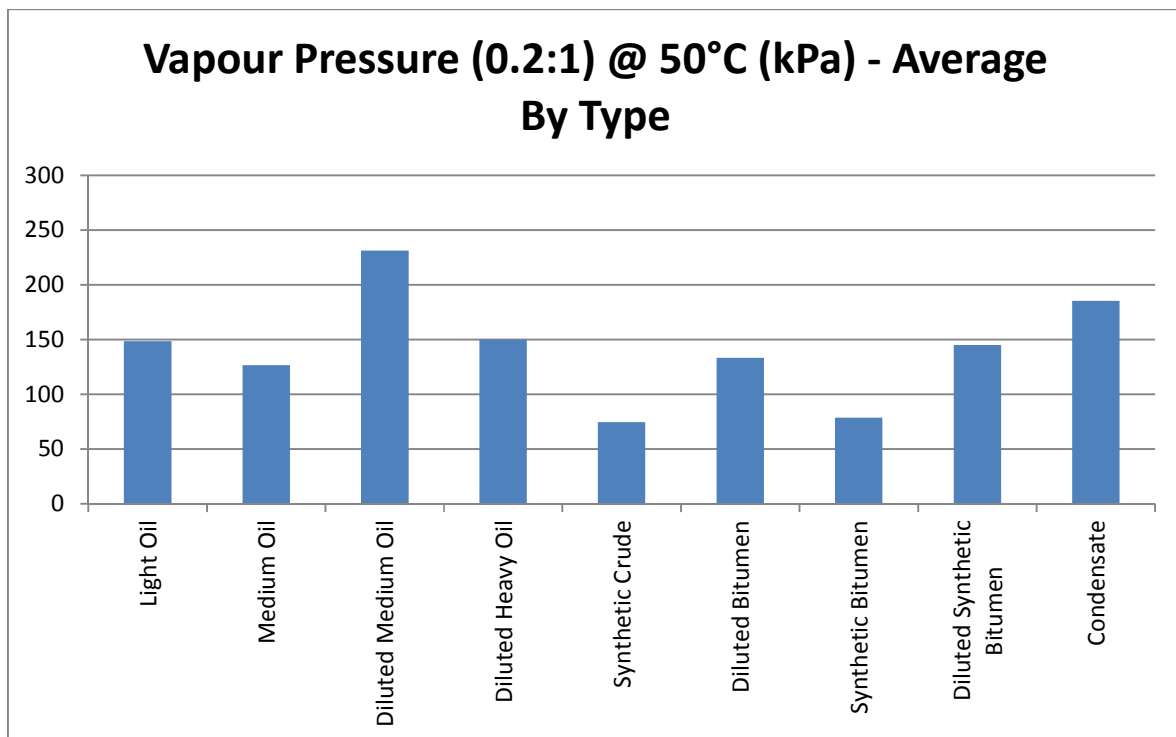


Figure 67: ASTM D7169 Chromatogram of a Diluted Synthetic Bitumen, FL14\_1881-021

**8.8 Vapour Pressure at 50°C**

**8.8.1 Vapour Pressure at a V/L Ratio of 0.2:1 and 50°C, ASTM D6377**

All samples collected into cylinders were submitted for vapour pressure measurement at 50°C and a V/L ratio of 0.2:1 using ASTM D6377. The average vapour pressure is shown in Figure 68. The average, minimum and maximum vapour pressures and the standard deviation for each oil type are shown in Table 12.



**Figure 68: Average Vapour Pressure (0.2:1) @ 50°C by Crude Oil Type**

The average vapour pressures (V/L 0.2:1 & 50°C) of the crude oils follow the pattern expected based on composition. Condensate, with the highest percentage of light ends and the least amount of C25+ residue has the highest average vapour pressure. Synthetic crude and synthetic bitumen, with the lowest percentage of light ends have the lowest vapour pressures. All other samples fall in the range between condensate and synthetic crude according to their composition. The effect of diluent on the vapour pressure is shown by the increased vapour pressure of the diluted samples as compared to the undiluted samples.

# ANNEX B - AITF REPORT (EN)



**Table 12: Average, Minimum, Maximum Vapour Pressure (V/L 0.2:1, 50°C) and Standard Deviation – By Crude Oil Type**

Crude Oil Type	Average Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Minimum Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Maximum Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	SD
Light Oil	149	89	301	46
Medium Oil	127	31	528	129
Diluted Medium Oil*	231			
Diluted Heavy Oil	150	148	151	2
Synthetic Crude	75	73	76	2
Diluted Bitumen	133	81	161	31
Synthetic Bitumen*	79			
Diluted Synthetic Bitumen*	145			
Condensate	185	139	273	43

\*Single sample only

To further illustrate the relationship between light ends and vapour pressure, the samples were grouped into five vapour pressure ranges and the sum of C1-C4, C1-C6, and C1-C8 and the average vapour pressure for each range was calculated. The results are shown in Table 13.

**Table 13: Sum of Light Ends vs. Vapour Pressure**

Vapour Pressure Range (kPa)	Sum of C1-C4 (mass%)	Sum of C1-C6 (mass%)	Sum of C1-C8 (mass%)	Average Vapour Pressure (0.2:1) @ 50°C, ASTM D6377
0-100	0.7	3.1	8.2	69.5
100-140	1.4	13.1	22.4	123.9
140-160	2.2	14.1	26.8	149.4
160-200	2.4	23.8	38.5	177.3
200-550	5.4	33.9	49.7	275.7

As shown in Figure 69, the vapour pressure is affected by both the amount and the composition of the light ends. Hydrocarbons in the range of C1 to C4 have the most significant effect on vapour pressure; a small increase in C1 to C4 has a greater effect than an increase in the range of C1 to C6 or C1 to C8.

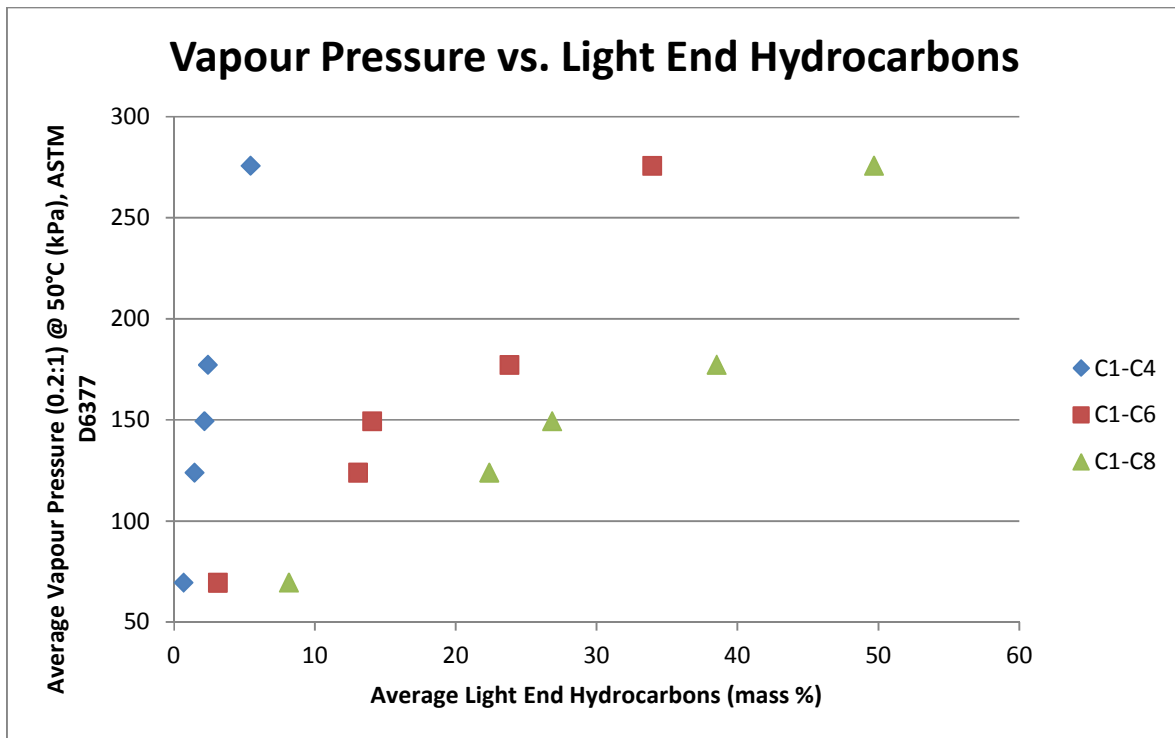


Figure 69: Vapour Pressure vs. Light End Hydrocarbons, Ordered by Vapour Pressure

The distribution of vapour pressures by crude type is shown in Figure 70.

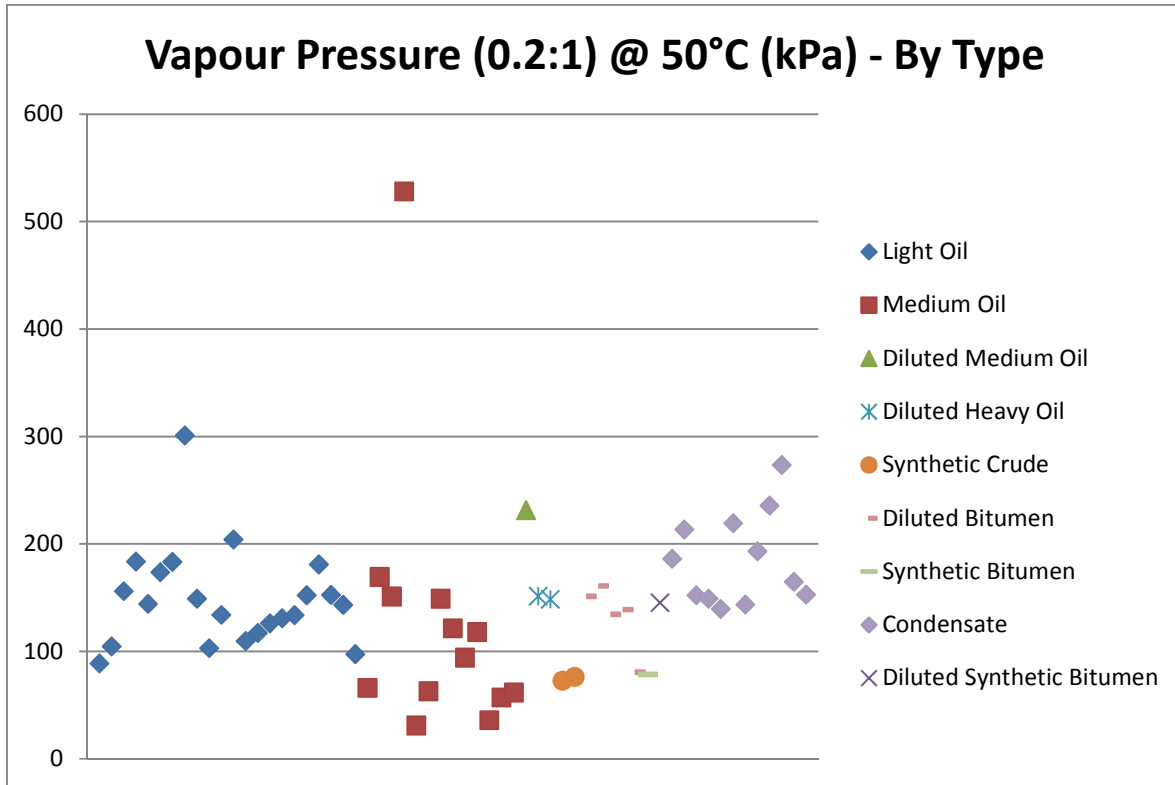


Figure 70: Distribution of Vapour Pressure (0.2:1) @ 50°C by Crude Oil Type

---

Sample FL14\_1881-244, a medium oil had the highest vapour pressure at 50°C, 527.9kPa. The oil from this site is loaded onto trucks from the sales tank and trucked to another facility for additional processing. However, the sample was collected from the transfer line between the free water separator and the treater, as this was the sampling point the technologist was directed to use by the site operator. Gases present in the oil would be at higher concentration at this location. Both water and gas are removed from the oil in the treater before the oil is transferred to the sales tank. In this case, the sample collected may not have been representative of the product transported. The product transported likely has a lower vapour pressure. A schematic of the battery is shown in Figure 71.

This battery uses an enhanced oil recovery process. During primary production, the emulsion of oil and water flows to surface (through natural formation pressure), or is pumped to surface. Over time, the reservoir pressure drops as fluid is extracted from the formation. Eventually the well will no longer produce at an economic rate. Produced water is injected back into the producing formation to maintain the reservoir pressure and “enhance” the recovery of the oil. Solution gas produced along with the oil is extracted and used as fuel in the treating process where oil and gas are separated from water. Solution gas is dissolved gas in wellbore or reservoir fluids that will remain in solution until the pressure or temperature conditions change, at which time it may break out of solution to become free gas. The presence of solution gas in this sample may have contributed to the high vapour pressure. According to the C1 to C25+ composition, this sample had the highest mass % of CO<sub>2</sub> and C1 of all samples collected, 0.071% and 0.258% respectively. This sample also had the second highest gas/oil ratio (GOR), 6.79, of all samples collected.

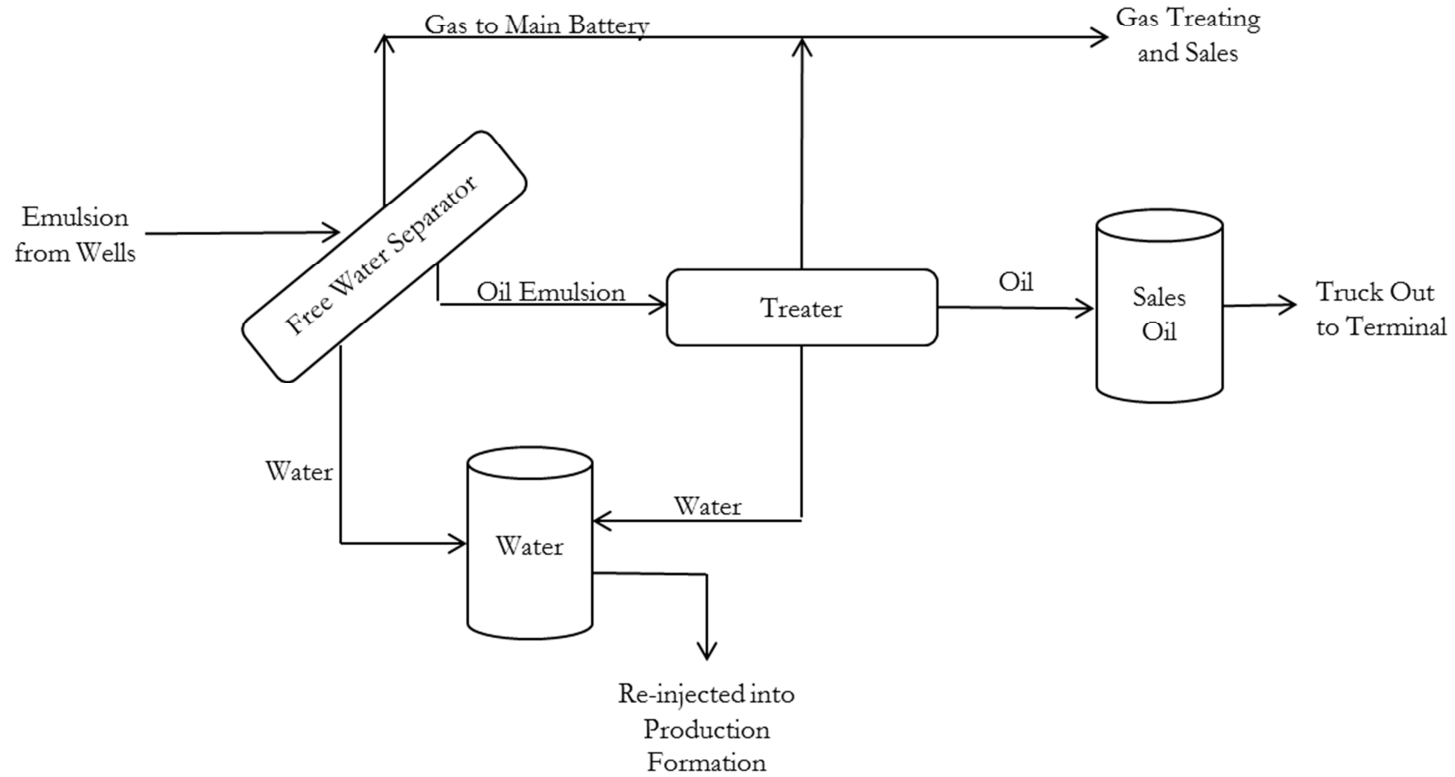


Figure 71: Sample FL14\_2881-244 Battery Configuration



Sample FL14\_1881-178, a light oil, had the second highest vapour pressure, 300.8kPa. The results for this sample indicate that sampling conditions such as ambient temperature and battery operating parameters such as treater temperature have an impact on vapour pressure. This sample was Bakken oil collected from a sales tank at a battery in Saskatchewan. Prior to the sales tank, the oil goes through a treater to remove gas and water. The treater accelerates separation by using heat, pressure, and sometimes chemicals and electrical mechanisms. The treater separates streams of gas, pipeline-specification oil and often disposal-quality water. However, the burner on the treater at this battery was off, which may have resulted in incomplete separation of gas from the oil. As well, the ambient temperature at the time of sample collection was  $-15^{\circ}\text{C}$ . Sample collection at this temperature would have helped to prevent the loss of any light ends present, especially C1 and C2, which have a significant effect on vapour pressure. According to the C1 to C24 composition, this sample has the highest mass % of C1 and C2 of all the light oils collected, 0.022% and 0.275% respectively. This sample also had the highest GOR of all samples collected, 10.74. As the oil is loaded onto trucks from the sales tank, this sample was representative of the product transported.

### **8.8.2 Vapour Pressure at a V/L Ratio of 0.02:1 and $50^{\circ}\text{C}$ , Calculated**

The vapour pressure of the crude oils at V/L 0.02: 1 and  $50^{\circ}\text{C}$  was calculated from the measured values at V/L 0.2:1 and  $50^{\circ}\text{C}$  using the Peng-Robinson equation of state. Vapour pressure at V/L 0.02:1 and  $50^{\circ}\text{C}$  is significant in that the V/L corresponds to the outage in rail cars, which is  $\sim 5\%$ . The comparison between the values at 0.02:1 and 0.2:1 is shown in Figure 72 and Table 14.

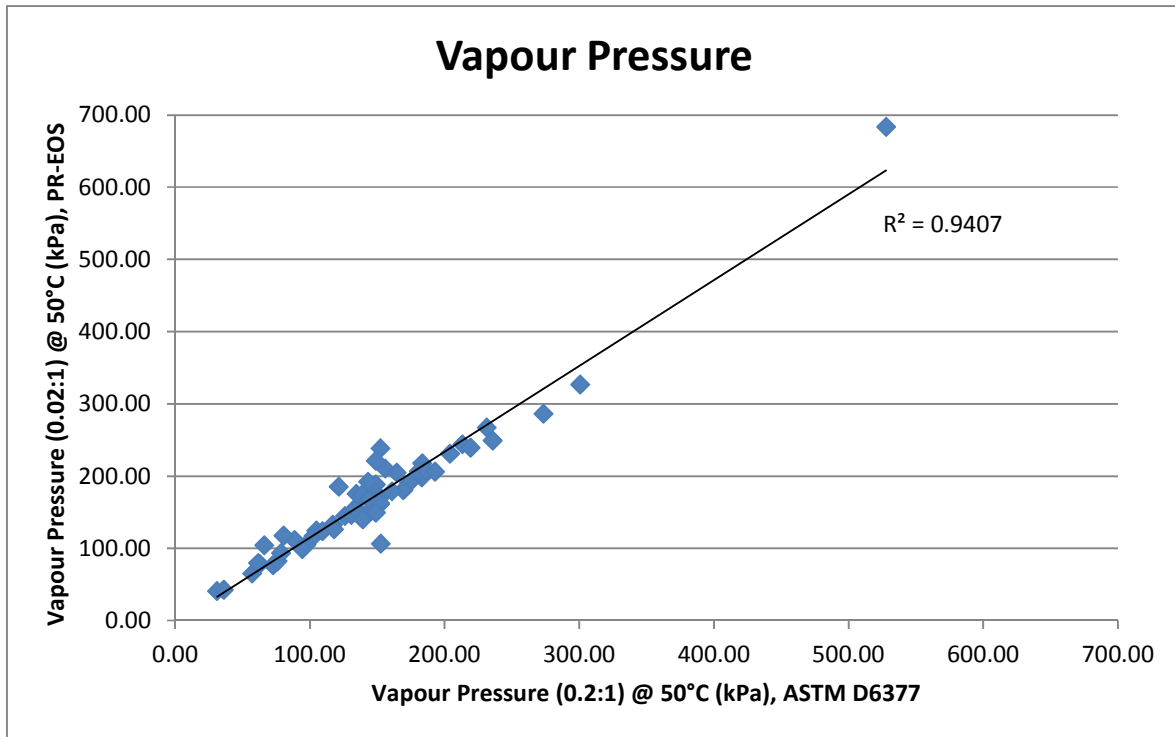


Figure 72: Vapour Pressure @ 50°C, V/L 0.02:1 (PR-EOS) vs. V/L 0.2:1 (ASTM D6377)

As can be seen in Figure 72, the difference between the vapour pressure at 0.02:1 and 0.2:1 at 50°C is not very large. These two V/L ratios are close to the bubble point pressure (V/L 0) and a large difference is not expected. As expected, reduction of the V/L ratio to 0.02:1 from 0.2:1 resulted in an increase in vapour pressure; however the increase was not large enough to result in of any samples crossing the 300kPa threshold.

# ANNEX B - AITF REPORT (EN)



Table 14: Vapour Pressure at 50°C, V/L 0.02:1 (PR-EOS) and V/L 0.2:1 (ASTM D6377)

LIMS #	Type	Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (0.02:1) @ 50°C (kPa), PR-EOS	Δ(kPa)
FL14_1881-049	Light Oil	88.70	111.80	23.10
FL14_1881-057	Light Oil	104.70	124.60	19.90
FL14_1881-061	Light Oil	155.90	210.60	54.70
FL14_1881-122	Light Oil	183.50	217.90	34.40
FL14_1881-146	Light Oil	144.10	151.00	6.90
FL14_1881-150	Light Oil	173.70	190.40	16.70
FL14_1881-166	Light Oil	183.10	198.20	15.10
FL14_1881-178	Light Oil	300.80	327.00	26.20
FL14_1881-240	Light Oil	149.00	188.50	39.50
FL14_1881-252	Light Oil	102.80	116.80	14.00
FL14_1881-276	Light Oil	133.90	155.80	21.90
FL14_1881-069	Light Oil	204.00	231.20	27.20
FL14_1881-094	Light Oil	109.50	123.90	14.40
FL14_1881-098	Light Oil	117.10	132.90	15.80
FL14_1881-102	Light Oil	126.00	144.80	18.80
FL14_1881-106	Light Oil	130.60	146.20	15.60
FL14_1881-134	Light Oil	133.60	155.30	21.70
FL14_1881-170	Light Oil	152.20	161.10	8.90
FL14_1881-174	Light Oil	181.00	206.60	25.60
FL14_1881-204	Light Oil	152.50	238.30	85.80
FL14_1881-208	Light Oil	143.20	192.50	49.30
FL14_1881-292	Light Oil	97.50	105.20	7.70
FL14_1881-142	Medium Oil	66.20	104.40	38.20
FL14_1881-154	Medium Oil	169.40	180.50	11.10
FL14_1881-162	Medium Oil	151.10	160.40	9.30
FL14_1881-244	Medium Oil	527.90	683.80	155.90
FL14_1881-248	Medium Oil	31.10	41.10	10.00
FL14_1881-256	Medium Oil	62.80	78.60	15.80
FL14_1881-268	Medium Oil	148.90	221.40	72.50
FL14_1881-272	Medium Oil	121.50	185.20	63.70
FL14_1881-288	Medium Oil	94.30	99.30	5.00
FL14_1881-296	Medium Oil	118.00	126.50	8.50
FL14_1881-300	Medium Oil	36.00	42.80	6.80
FL14_1881-304	Medium Oil	57.10	65.20	8.10
FL14_1881-308	Medium Oil	61.60	79.80	18.20
FL14_1881-009	Diluted Medium Oil	231.30	267.40	36.10

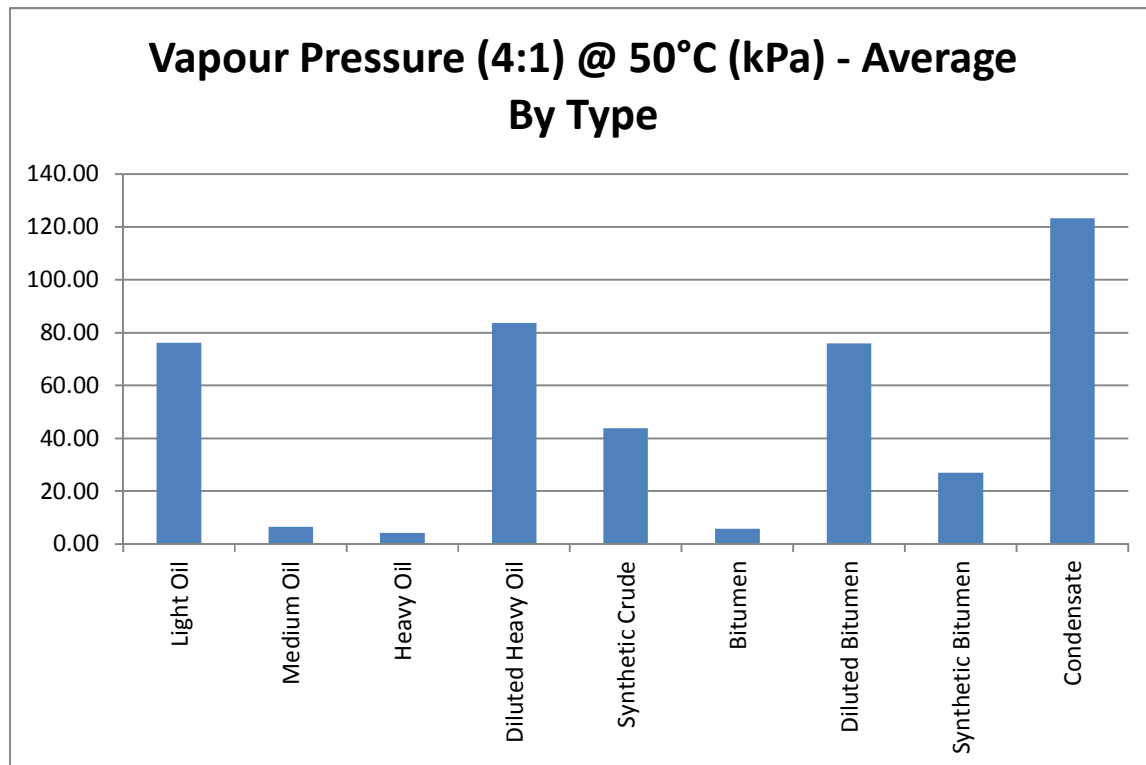
# ANNEX B - AITF REPORT (EN)



LIMS #	Type	Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (0.02:1) @ 50°C (kPa), PR-EOS	Δ(kPa)
FL14_1881-001	Diluted Heavy Oil	151.30	171.90	20.60
FL14_1881-013	Diluted Heavy Oil	148.40	163.20	14.80
FL14_1881-220	Synthetic Crude	72.70	76.90	4.20
FL14_1881-224	Synthetic Crude	76.20	82.50	6.30
FL14_1881-005	Diluted Bitumen	151.30	169.00	17.70
FL14_1881-017	Diluted Bitumen	161.00	179.00	18.00
FL14_1881-192	Diluted Bitumen	134.60	175.50	40.90
FL14_1881-196	Diluted Bitumen	138.80	174.80	36.00
FL14_1881-200	Diluted Bitumen	80.50	117.60	37.10
FL14_1881-232	Synthetic Bitumen	78.60	93.70	15.10
FL14_1881-021	Diluted Synthetic Bitumen	145.10	168.90	23.80
FL14_1881-025	Condensate	186.20	207.90	21.70
FL14_1881-073	Condensate	213.40	244.00	30.60
FL14_1881-114	Condensate	152.10	162.70	10.60
FL14_1881-118	Condensate	149.10	149.50	0.40
FL14_1881-126	Condensate	139.30	140.30	1.00
FL14_1881-130	Condensate	219.20	239.30	20.10
FL14_1881-138	Condensate	143.60	167.60	24.00
FL14_1881-228	Condensate	192.90	206.10	13.20
FL14_1881-280	Condensate	235.70	249.20	13.50
FL14_1881-284	Condensate	273.40	286.50	13.10
FL14_1881-090	Condensate	164.50	204.90	40.40
FL14_1881-110	Condensate	152.80	168.3	15.5

**8.8.3 Vapour Pressure at a V/L Ratio of 4:1 and 50°C, ASTM D323M**

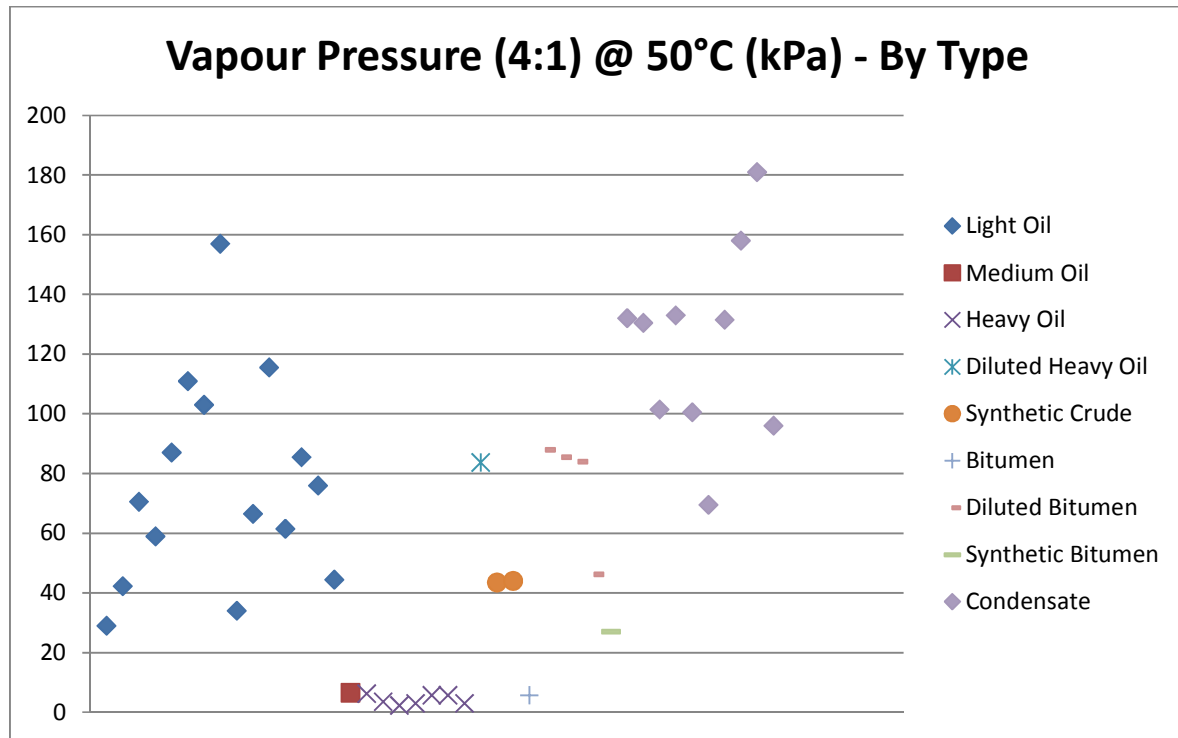
The vapour pressure at a V/L of 4:1 and 50°C for the thirty three samples with the highest proportion of light ends in each region, as determined by compositional analysis, was measured by ASTM D323M. This method was also used for the samples that were too viscous to be sampled into cylinders. These samples were conditioned at 20°C prior to analysis so that the samples would flow. Light ends in the heavy samples are present in low amounts and are not easily released because of reduced ease of diffusion among the dense molecules so the loss of light ends would be minimal. The average vapour pressure and the distribution of vapour pressures by crude type are shown below in Figures 73 and 74.



**Figure 73: Average Vapour Pressure (4:1) @ 50°C by Crude Oil Type**

The vapour pressure of the bitumen sample was reported but it should be noted that when cleaning the chamber after the run, it was found that it was only half full. While sampling the bitumen into the liquid chamber, the sample was poured over a period of 30 minutes and left to sit for an extra 5 minutes to make sure the liquid chamber was full. However it appears that

there was in fact air trapped in the chamber resulting in a less than full chamber as required by the method. This sample was too viscous and not appropriate for this method.



**Figure 74: Distribution of Vapour Pressure (4:1) @ 50°C by Crude Oil Type**

Sample FL14\_1881-285, a condensate, had the highest vapour pressure (4:1) at 50°C, 181kPa. This sample is a natural gasoline condensate of North Dakota origin collected at a truck terminal in Saskatchewan. According to the C1 to C24 composition, this sample had 0.29% ethane, 0.35% isobutane and 9.24% butane which would account for the high vapour pressure. Sample FL14\_1881-281, a condensate, had the second highest vapour pressure (4:1) at 50°C, 158kPa. This sample is also a natural gasoline condensate of North Dakota origin collected at a truck terminal in Saskatchewan. According to the C1 to C24 composition, this sample has 10.10% butane, which would contribute to the high vapour pressure.

Sample FL14\_1881-179, a light oil, had the third highest vapour pressure (4:1) at 50°C, 157kPa. This sample is the matching atmospheric sample of FL14\_1881-178, which had the second the highest vapour pressure as determined by ASTM D6377. Sample collection at -15°C and the fact that the bottle was not opened until testing would have helped to prevent the loss of light ends,

# ANNEX B - AITF REPORT (EN)



especially C1 and C2, which have a significant effect on vapour pressure. These three samples also had some of the highest vapour pressures as measured by ASTM D6377 at V/L 0.2:1 and 50°C.

The vapour pressure of eight samples was determined by ASTM D6377 using a V/L ratio of 4:1 @ 50°C to enable a comparison with ASTM D323M. The results are shown below in Figure 75 and Table 15.

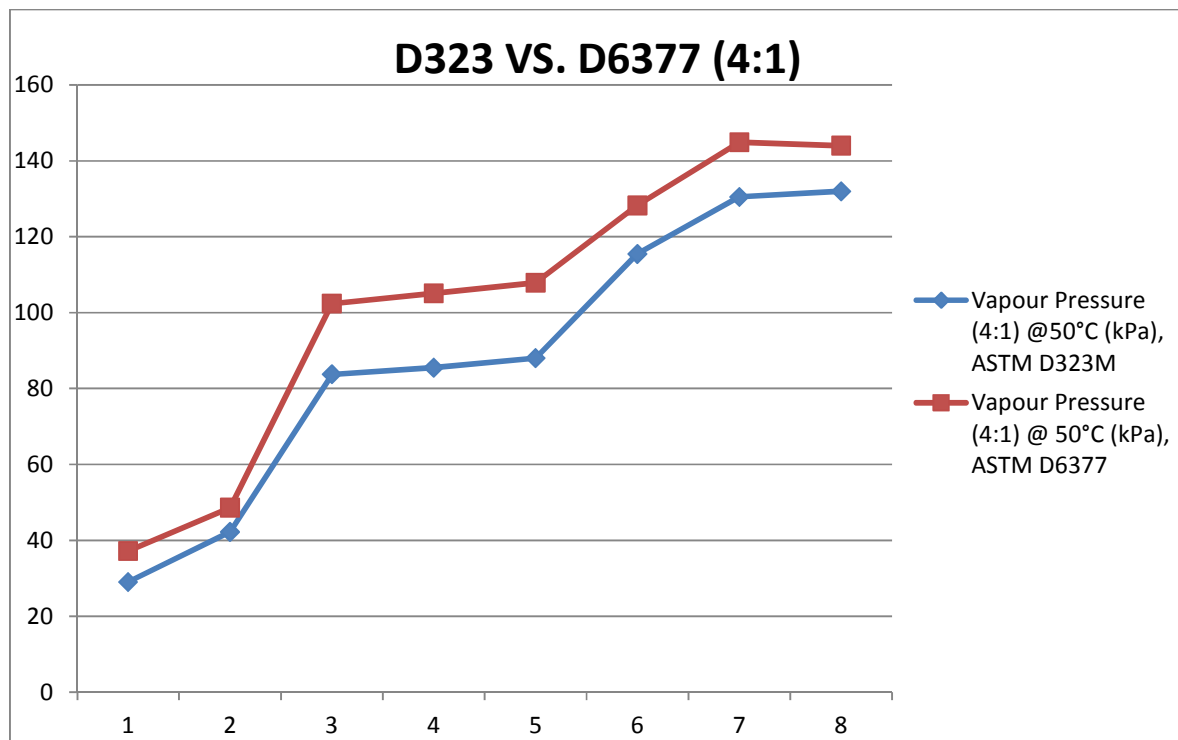


Figure 75: Comparison of ASTM D6377 and ASTM D323M Vapour Pressures (4:1) @ 50°C

# ANNEX B - AITF REPORT (EN)



**Table 15: Difference in Vapour Pressure (4:1) @ 50°, ASTM D6377 vs. ASTM D323M**

LIMS#	Region	Sample Type	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D323M	Δ(kPa)
FL14_1881-026	AB	condensate	144	132	12.0
FL14_1881-074	AB	condensate	144.9	130.5	14.4
FL14_1881-006	AB	dilbit	107.9	88	19.9
FL14_1881-018	AB	dilbit	105.1	85.5	19.6
FL14_1881-002	AB	heavy oil, diluted	102.4	83.75	18.7
FL14_1881-050	SK	light oil	37.2	29	8.2
FL14_1881-058	SK	light oil	48.6	42.25	6.4
FL14_1881-070	AB	light oil, sour	128.3	115.5	12.8

As sample collection for ASTM D323M is into open containers and air saturation steps are included in the method, there is a loss of light end components. A sample conditioning temperature of 0°C is not low enough to prevent components such as C1-C2 and gases such as CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S from outgassing during sample transfer or the air saturation steps. The potential loss of light ends is eliminated in ASTM D6377 as the sample is introduced into the instrument directly from the floating piston cylinder and the measuring chamber is sealed. Due to these factors, vapour pressure as determined by ASTM D323M tends to be lower than the vapour pressure determined by ASTM D6377. The difference in vapour pressure between the two methods will depend on the concentration and composition of light ends in the sample (CCQTA, 2014). Samples with a high percentage of light ends or more C1 and C2 as compared to C4 will give the largest differences.

Samples FL14\_1881-050 and -058 had the smallest difference in vapour pressure between the two methods, due to their composition. Table 16 below shows the fixed gas and light ends (C1 to C4) composition of the samples for which vapour pressure was measured at V/L 4:1 and 50°C by both methods. Samples FL14\_1881-050 and -058 have some of the lowest C1 to C4 and C1 to C2 percentages but the fixed gas composition also has an effect on vapour pressure. Both samples have <0.001 mass % CO<sub>2</sub> and the lowest amounts of N<sub>2</sub>, 0.004 and 0.003 mass % respectively, which would explain why the difference in vapour pressures between the two methods for these samples is small.



# ANNEX B - AITF REPORT (EN)



Table 16: Fixed Gas and Light End Composition of Samples for which Vapour Pressure was measured at V/L 4:1 and 50°C by ASTM D6377 and ASTM D323M

LIMS #	FL14_1881-026	FL14_1881-074	FL14_1881-006	FL14_1881-018	FL14_1881-002	FL14_1881-050	FL14_1881-058	FL14_1881-070
Mass %	Condensate	Condensate	Dilbit	Dilbit	Diluted Heavy Oil	Light oil	Light oil	Light oil
<b>CO<sub>2</sub></b>	0.003	0.001	0.017	0.006	0.005	<0.001	<0.001	0.003
<b>CO</b>	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
<b>H<sub>2</sub>S</b>	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
<b>He</b>	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
<b>H<sub>2</sub></b>	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
<b>O<sub>2</sub></b>	0.011	0.012	0.001	<0.001	0.001	<0.001	<0.001	<0.001
<b>N<sub>2</sub></b>	0.037	0.044	0.007	0.006	0.008	0.004	0.003	0.015
<b>C1</b>	0.002	0.011	0.007	0.012	0.007	0.012	0.014	0.009
<b>C2</b>	0.006	0.023	0.004	0.007	0.006	0.01	0.01	0.037
<b>C3</b>	0.036	0.198	0.056	0.054	0.07	0.11	0.19	0.363
<b>iC4</b>	0.316	0.314	0.315	0.165	0.388	0.099	0.189	1.88
<b>nC4</b>	3.25	3.17	1.13	0.72	1.77	0.396	0.686	3.12
<b>Sum of Fixed Gases</b>	0.051	0.057	0.026	0.012	0.014	0.004	0.003	0.018
<b>Sum of C1-C2</b>	0.008	0.034	0.011	0.019	0.013	0.022	0.024	0.046
<b>Sum of C1-C4</b>	3.61	3.716	1.512	0.958	2.241	0.627	1.089	5.409

#### 8.8.4 Calculated Vapour Pressure at a V/L Ratio of 4:1 and 50°C

Using the Peng Robinson equation of state, the vapour pressure at a V/L ratio of 4:1 and 50°C was calculated for the thirty-three samples submitted for ASTM D323M. Table 17 below shows the difference between the calculated and measured vapour pressure (ASTM D6377) for eight samples. The difference between the values is small, indicating that the model fits the data well.

**Table 17: Vapour Pressure (4:1) @ 50°, ASTM D6377 vs. PR-EOS**

LIMS #	Sample Type	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (4:1) @ 50°C (kPa), PR-EOS	Δ Vapour Pressure (kPa)
FL14_1881-073	Condensate	144.9	151	-6.1
FL14_1881-069	Light Oil	128.3	136.8	-8.5
FL14_1881-057	Light Oil	48.6	54.9	-6.3
FL14_1881-049	Light Oil	37.2	40.8	-3.6
FL14_1881-025	Condensate	144	144.7	-0.7
FL14_1881-017	Diluted Bitumen	105.1	111.5	-6.4
FL14_1881-005	Diluted Bitumen	107.9	106.5	1.4
FL14_1881-001	Diluted Heavy Oil	102.4	103.7	-1.3

#### 8.8.5 Comparison of Vapour Pressures (50°C) at Each V/L Ratio

The measured and calculated vapour pressures at 50°C for the thirty-three samples with the highest proportion of light ends in each region, as determined by compositional analysis, at V/L ratios of 0.02:1, 0.2:1 and 4:1 are shown in Figure 76 and Table 18.

Two main observations can be made from this vapour pressure data:

1. The vapour pressure decreases as the V/L ratio increases which is the expected result.
2. The vapour pressure as determined by ASTM D323M is consistently lower than both the calculated and measured vapour pressure by ASTM D6377.

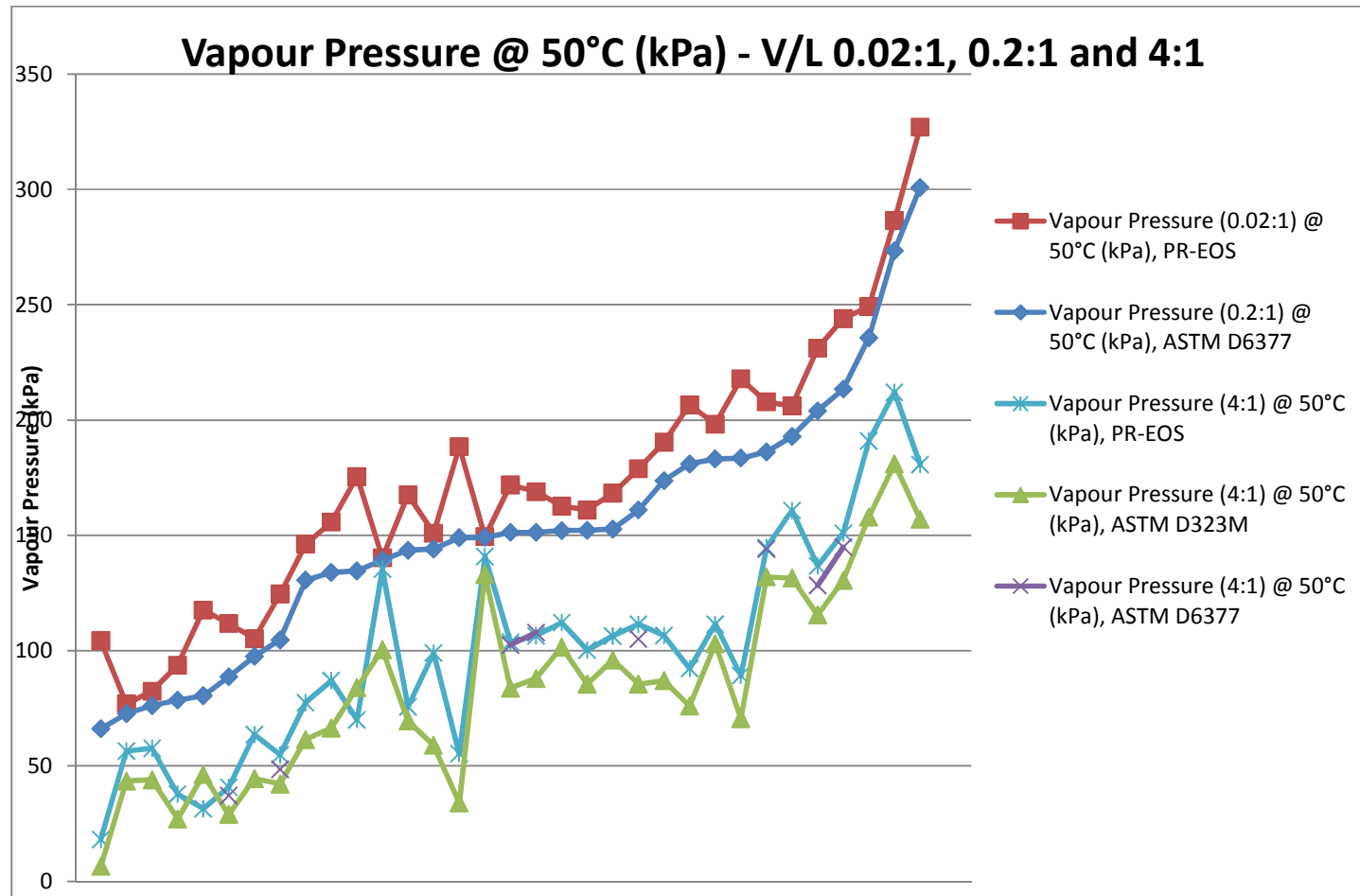


Figure 76: Measured and Calculated Vapour Pressures (50°C)

# ANNEX B - AITF REPORT (EN)

Table 18: Vapour Pressure (50°), V/L 0.02:1, 0.2:1 and 4:1

LIMS #	Type	Vapour Pressure (0.02:1) @ 50°C (kPa), PR-EOS	Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (4:1) @ 50°C (kPa), PR-EOS	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D323M	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D6377
FL14_1881-142	Medium Oil	104.40	66.20	18.2	6.5	
FL14_1881-220	Synthetic Crude	76.90	72.70	56.5	43.5	
FL14_1881-224	Synthetic Crude	82.50	76.20	57.7	44.0	
FL14_1881-232	Synthetic Bitumen	93.70	78.60	37.8	27.0	
FL14_1881-200	Diluted Bitumen	117.60	80.50	31.5	46.3	
FL14_1881-049	Light Oil	111.80	88.70	40.8	29.0	37.2
FL14_1881-292	Light Oil	105.20	97.50	63.6	44.5	
FL14_1881-057	Light Oil	124.60	104.70	54.9	42.3	48.6
FL14_1881-106	Light Oil	146.20	130.60	77.5	61.5	
FL14_1881-276	Light Oil	155.80	133.90	87.0	66.5	
FL14_1881-192	Diluted Bitumen	175.50	134.60	70.1	84.0	
FL14_1881-126	Condensate	140.30	139.30	135.3	100.5	
FL14_1881-138	Condensate	167.60	143.60	75.7	69.5	
FL14_1881-146	Light Oil	151.00	144.10	99.0	59.0	
FL14_1881-240	Light Oil	188.50	149.00	55.3	34.0	
FL14_1881-118	Condensate	149.50	149.10	140.9	133.0	
FL14_1881-001	Diluted Heavy Oil	171.90	151.30	103.7	83.8	102.4
FL14_1881-005	Diluted Bitumen	169.00	151.30	106.5	88.0	107.9
FL14_1881-114	Condensate	162.70	152.10	112.2	101.5	
FL14_1881-170	Light Oil	161.10	152.20	100.3	85.5	
FL14_1881-110	Condensate	168.30	152.80	106.4	96.0	
FL14_1881-017	Diluted Bitumen	179.00	161.00	111.5	85.5	105.1
FL14_1881-150	Light Oil	190.40	173.70	106.6	87.0	

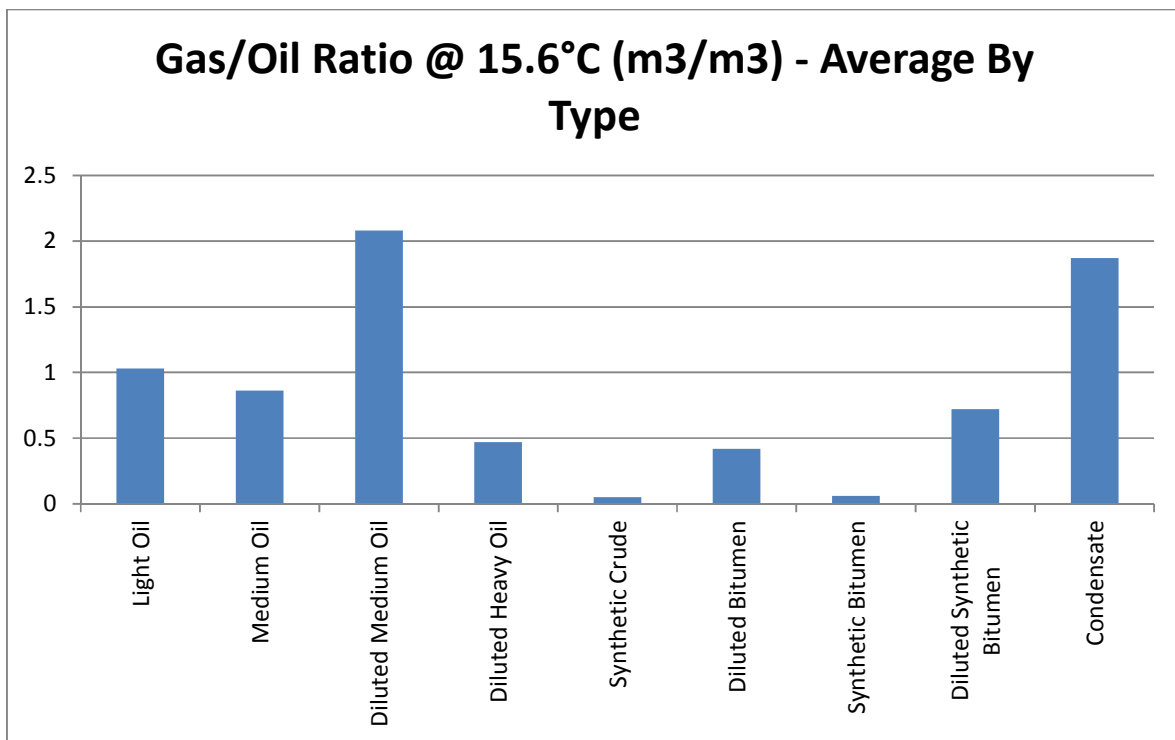
## ANNEX B - AITF REPORT (EN)



LIMS #	Type	Vapour Pressure (0.02:1) @ 50°C (kPa), PR-EOS	Vapour Pressure (0.2:1) @ 50°C (kPa), ASTM D6377	Vapour Pressure (4:1) @ 50°C (kPa), PR-EOS	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D323M	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D6377
FL14_1881-174	Light Oil	206.60	181.00	92.3	76.0	
FL14_1881-166	Light Oil	198.20	183.10	111.5	103.0	
FL14_1881-122	Light Oil	217.90	183.50	89.2	70.5	
FL14_1881-025	Condensate	207.90	186.20	144.7	132.0	144.0
FL14_1881-228	Condensate	206.10	192.90	160.8	131.5	
FL14_1881-069	Light Oil	231.20	204.00	136.8	115.5	128.3
FL14_1881-073	Condensate	244.00	213.40	151.0	130.5	144.9
FL14_1881-280	Condensate	249.20	235.70	191.0	158.0	
FL14_1881-284	Condensate	286.50	273.40	212.1	181.0	
FL14_1881-178	Light Oil	327.00	300.80	180.7	157.0	

**8.9 Gas Oil Ratio (GOR) and Flashed Gas GC Analysis**

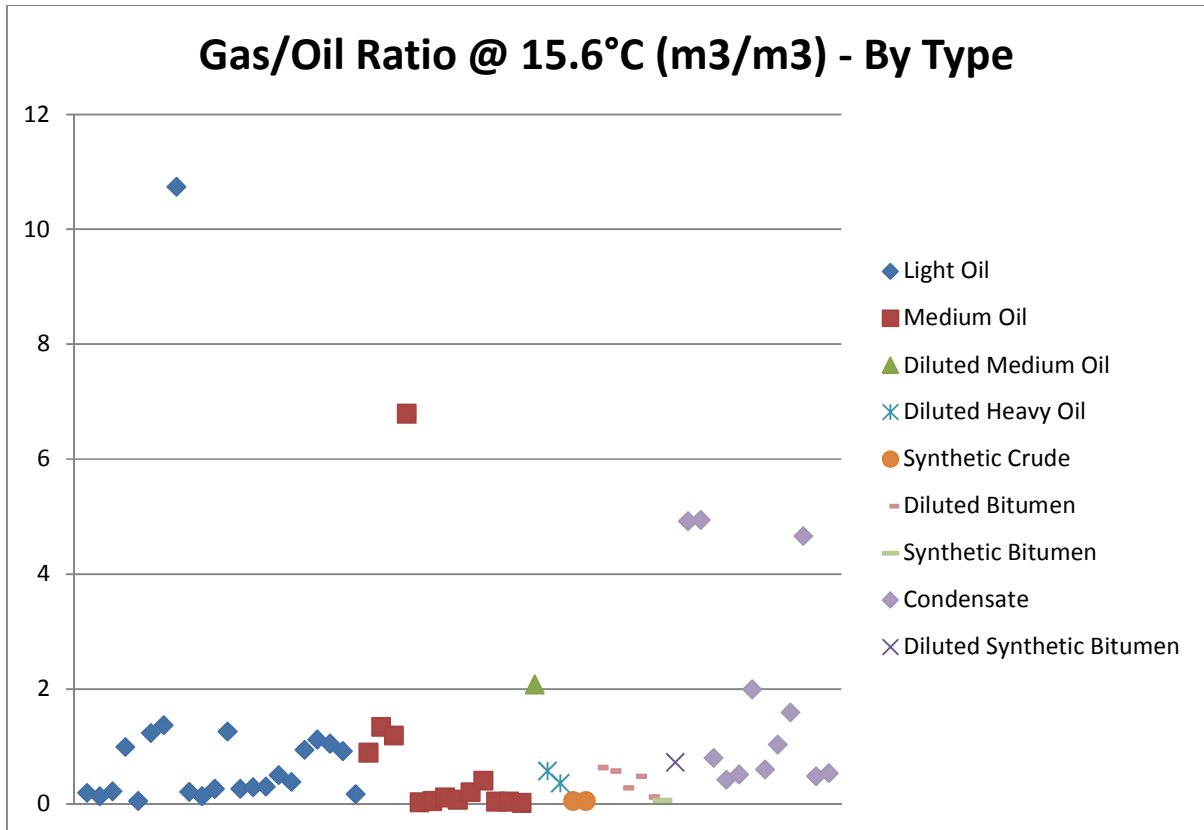
The gas oil ratio (GOR) is a measure of the volume of gas produced per volume of oil at defined conditions of temperature and pressure. The vapour phase above crude oil in a rail car or truck tank will contain gases that are in direct proportion to their relative volatilities and mole fractions in the liquid phase. It is the vapour phase that actually burns and the hazard presented by the vapour phase will depend on the amount of gas produced and its composition. Since the GOR flashes were done at atmospheric pressure and ambient laboratory temperature (23°C), the evolved gas composition from the GOR analysis is what would be in the vapour phase above that sample of crude oil under atmospheric pressure and equivalent temperature. High concentrations of light ends and or fixed gases will result in a higher GOR as more vapour will be produced. The average GOR and the distribution of GOR by crude type are shown below in Figures 77 and 78.



**Figure 77: Average GOR by Crude Oil Type**

The average GORs of the crude oils follow the pattern expected based on composition. Samples with the highest percentage of light ends, such as condensates, will have the highest GORs. Samples with the lowest percentage of light ends, such as synthetic crude and synthetic bitumen,

will have the lowest GORs. All other samples fall in the range between condensate and synthetic crude according to their composition. The effect of diluent on the GOR is shown by the increased GOR of the diluted samples as compared to the undiluted samples.



**Figure 78: Distribution of GOR by Crude Oil Type**

Variation of GOR within the crude types as seen in Figure 78 is due to differences in the light end and fixed gas composition (i.e. Carbon dioxide, hydrogen sulphide, helium, hydrogen, oxygen and nitrogen).

Sample FL14\_1881-178, a Bakken oil, had the highest GOR, 10.74, and one of the highest vapour pressures (0.2:1, 50°C), 300.8kPa. According to the C1 to C24 composition, this sample contained the highest mass percentage of propane, 3.73%. This sample was collected from a treater where the burner was not lit and the ambient temperature at the time of sampling was -15°C which helped to preserve the propane.

Sample FL14\_1881-244, a medium oil, had the second highest GOR, 6.76, and the highest vapour pressure (0.2:1, 50°C), 524.9kPa. This sample was collected from the free water separator (prior to the treater) at a battery where an enhanced oil recovery process was used and solution gas is produced along with the oil. This sample had the highest mass percentages of CO<sub>2</sub> and C1 according to the C1 to C24 composition, 0.071% and 0.158% respectively. The two condensates with the highest GORs had large percentages of iso-pentane and pentane. The condensate with the third highest GOR had the highest percentage of butane.

To further illustrate the relationship between light ends and GOR, the samples were grouped into five GOR ranges and the sum of C1-C4, C1-C6, and C1-C8 and the average GOR for each range was calculated. The results are shown in Table 19.

**Table 19: Sum of Light Ends vs. GOR**

GOR Range (m <sup>3</sup> /m <sup>3</sup> )	Sum of C1-C4 (mass %)	Sum of C1-C6 (mass %)	Sum of C1-C8 (mass %)	Average GOR (m <sup>3</sup> /m <sup>3</sup> )
0-0.15	0.783	3.158	8.083	0.07
0.15-0.4	1.314	6.943	15.752	0.26
0.4-0.8	1.708	10.734	21.360	0.55
0.8-1.2	2.092	15.035	27.057	0.99
1.2-11	4.710	31.047	46.713	3.58

As shown in Figure 79 below, the GOR is affected by both the amount of light ends and the composition of the light ends. Hydrocarbons in the range of C1 to C4 have the most significant effect on GOR, a small increase in concentration results in a large increase in GOR as compared to C1 to C6 and C1 to C8.



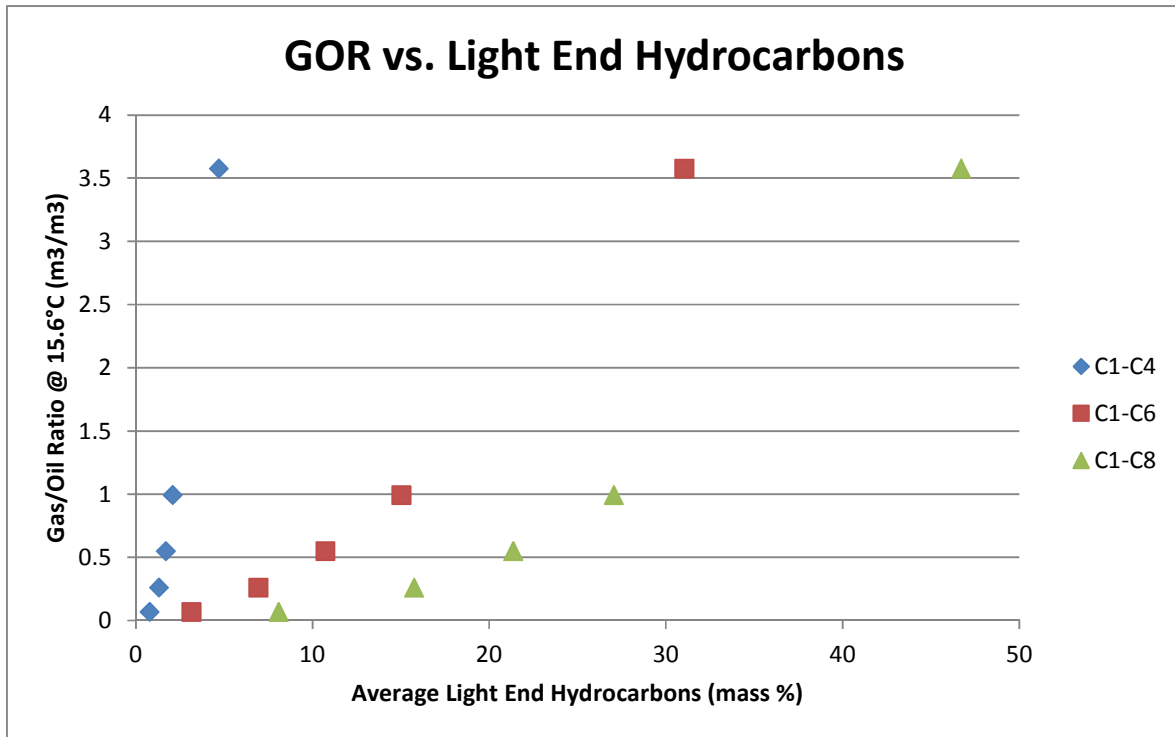


Figure 79: GOR vs. Light End Hydrocarbons, Ordered by GOR

The higher the GOR, the more vapour is produced, which, along with the composition of the vapour, has implications on the flammability of the vapour phase. The total composition of the flashed gas and the fixed gases present in the flashed gas are shown in Figures 80 to 97. The flashed gas composition represents the mass % of components in the vapour phase at the GOR conditions. The percentage of these components on a whole oil basis is much lower. The average total flashed gas and fixed gas compositions are presented for each oil type. Two additional graphs were produced for each oil type: in the first graph, the average total flashed gas compositions along with two samples at either end of the spectrum are shown, in the second graph, the average fixed gases present in the flashed gas are shown along with two samples at either end of the spectrum.

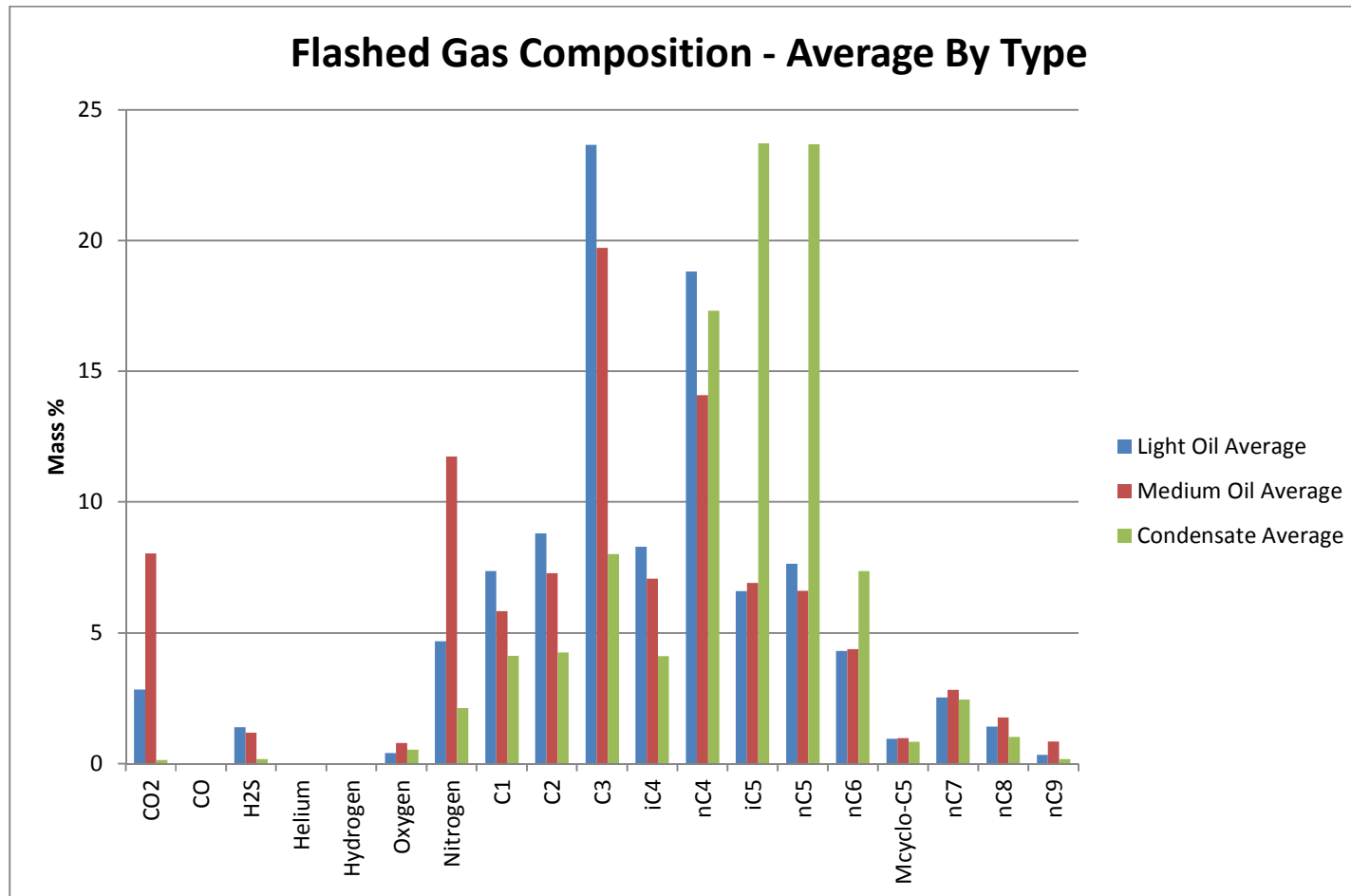


Figure 80: Average Light Oil, Medium Oil and Condensate Flashed Gas Composition

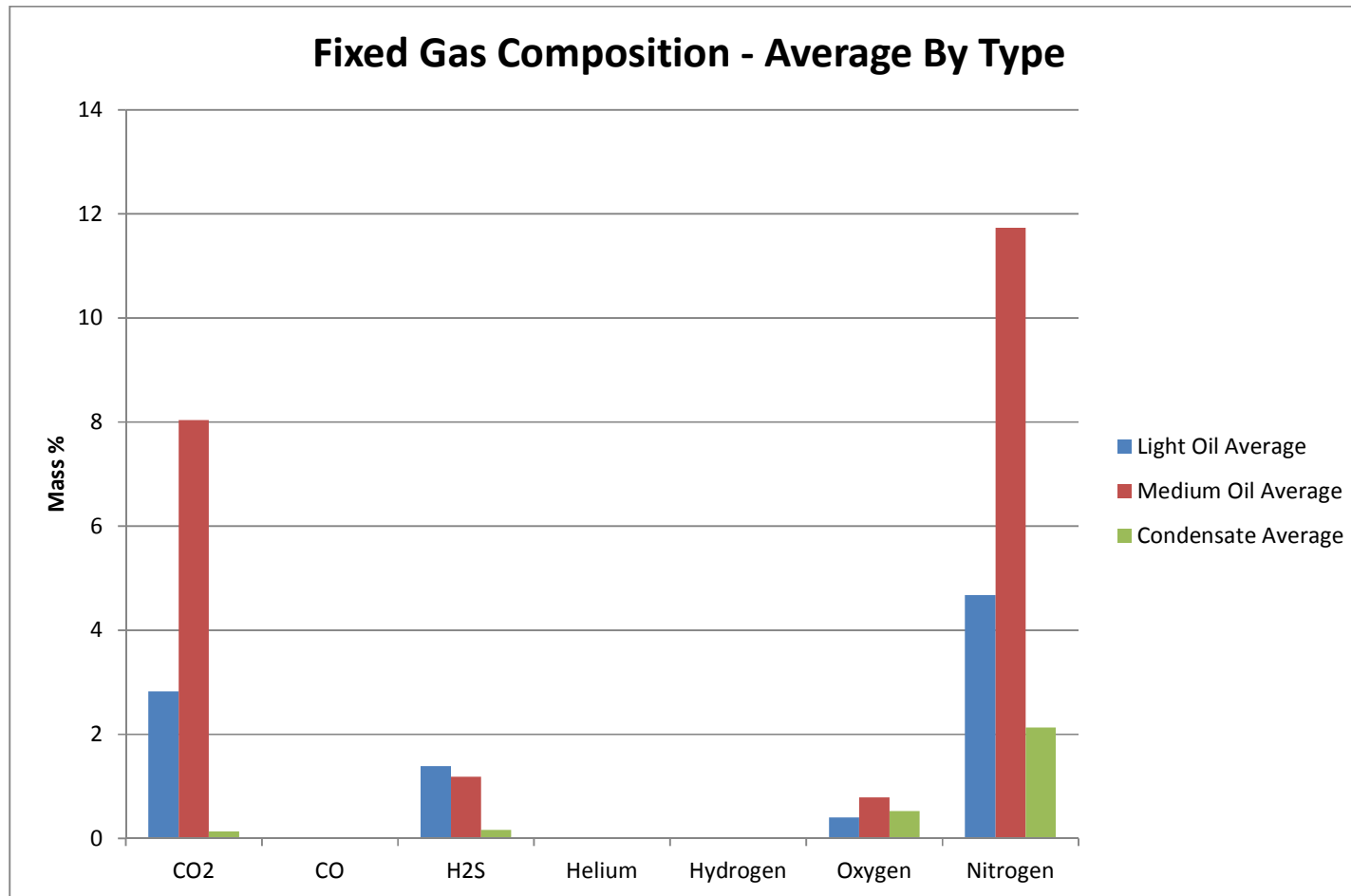


Figure 81: Average Light Oil, Medium Oil and Condensate Fixed Gas Composition

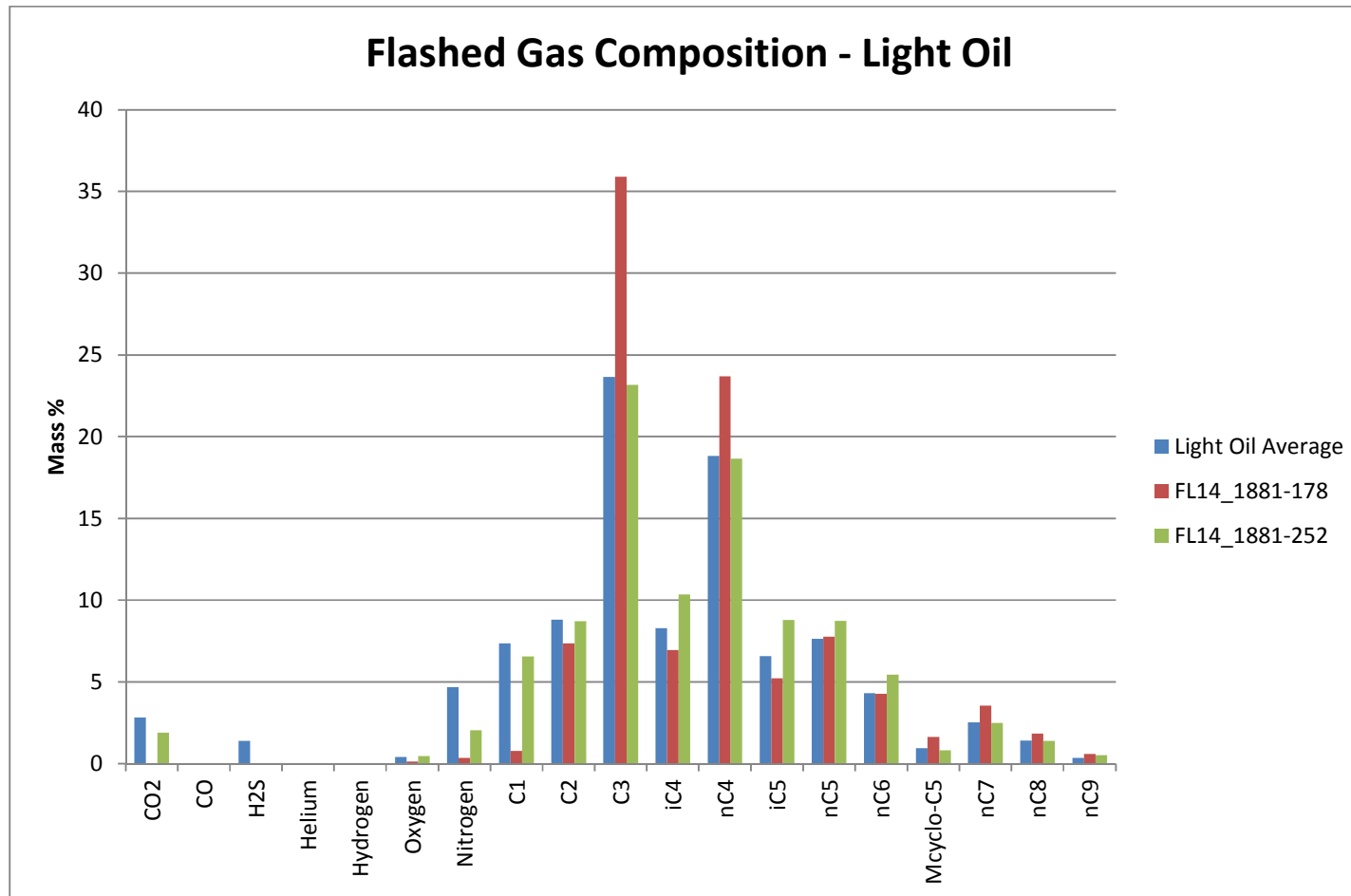


Figure 82: Light Oil Flashed Gas Composition

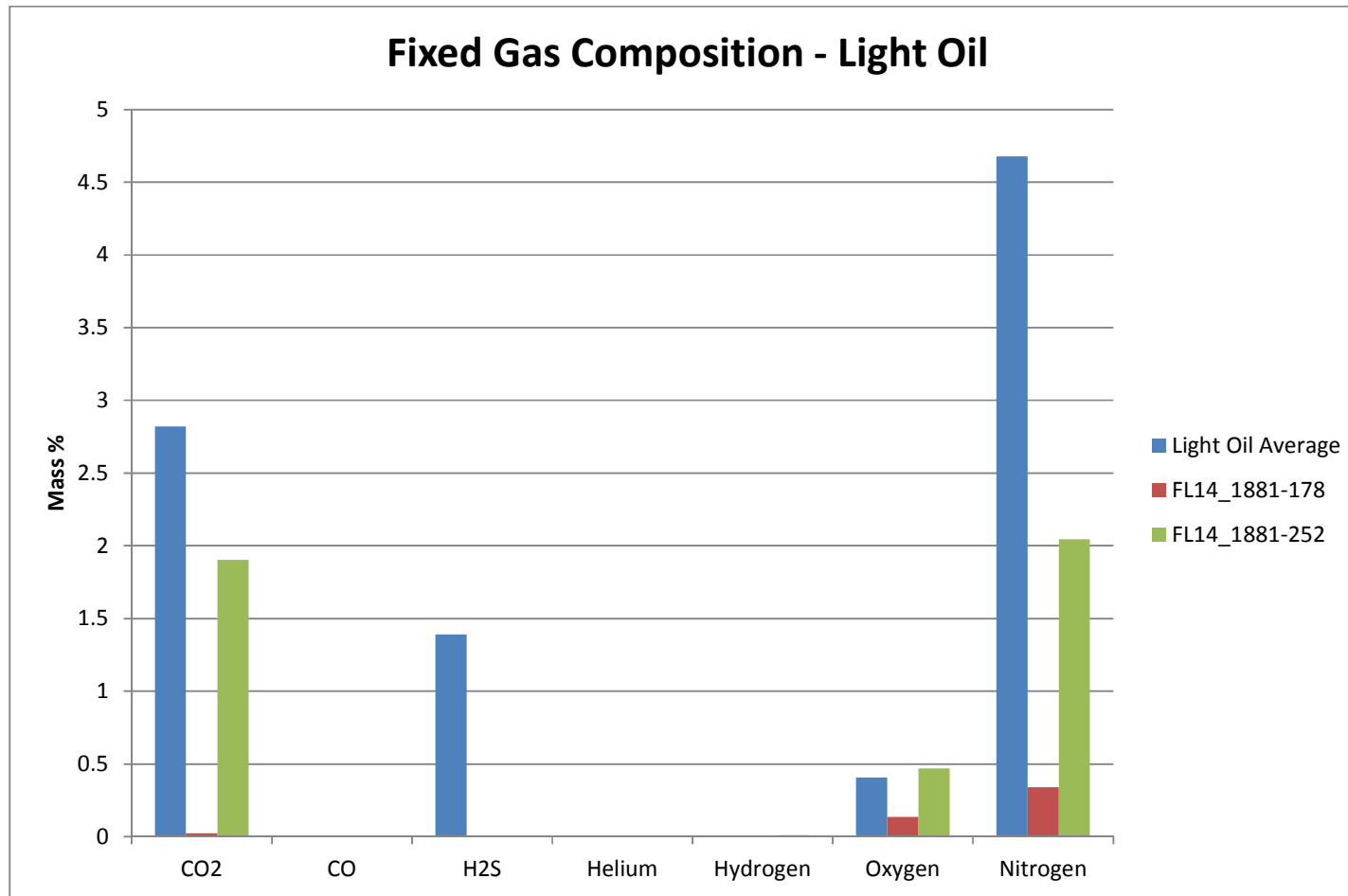


Figure 83: Light Oil Fixed Gas Composition

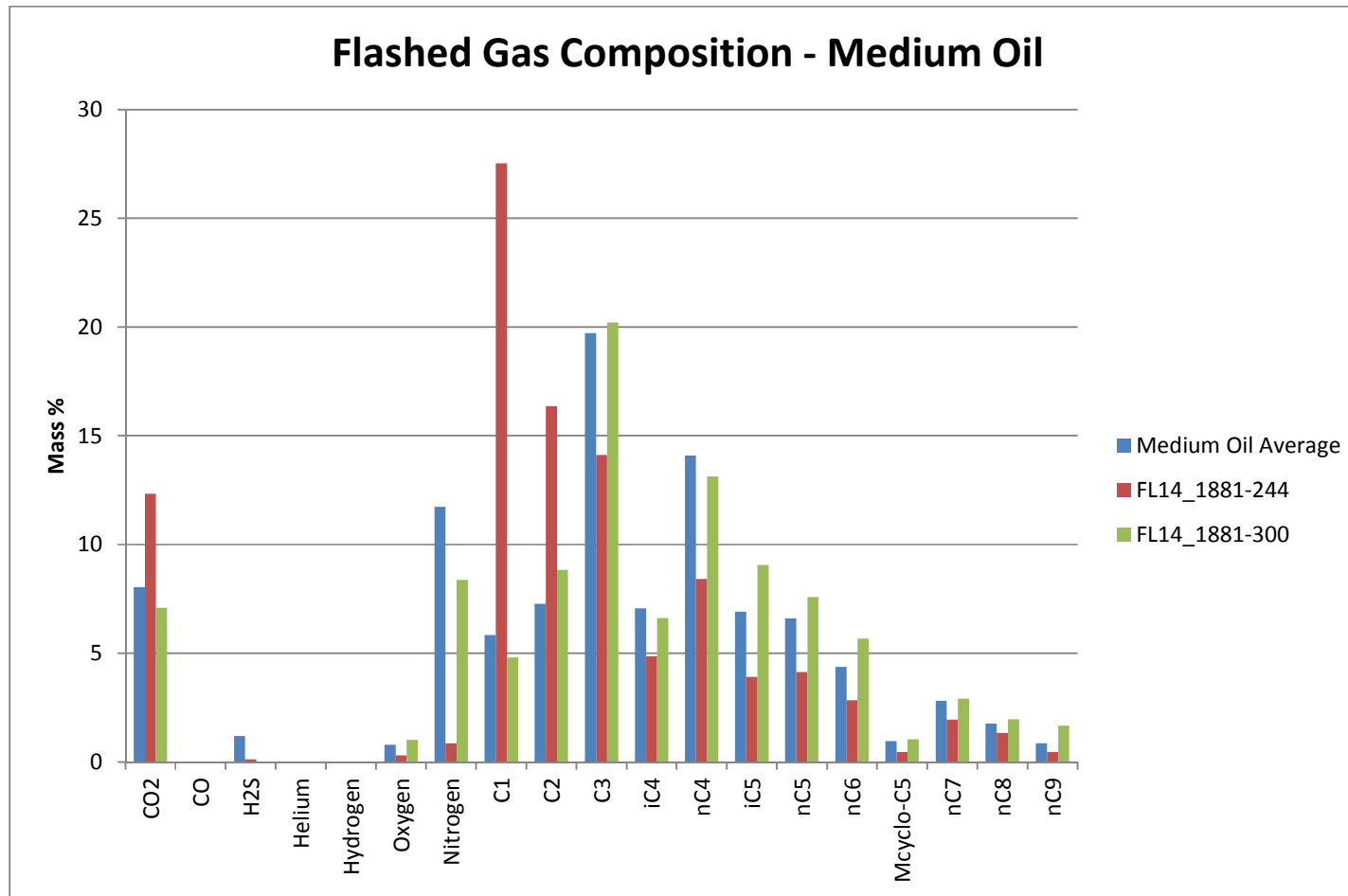


Figure 84: Medium Oil Flashed Gas Composition

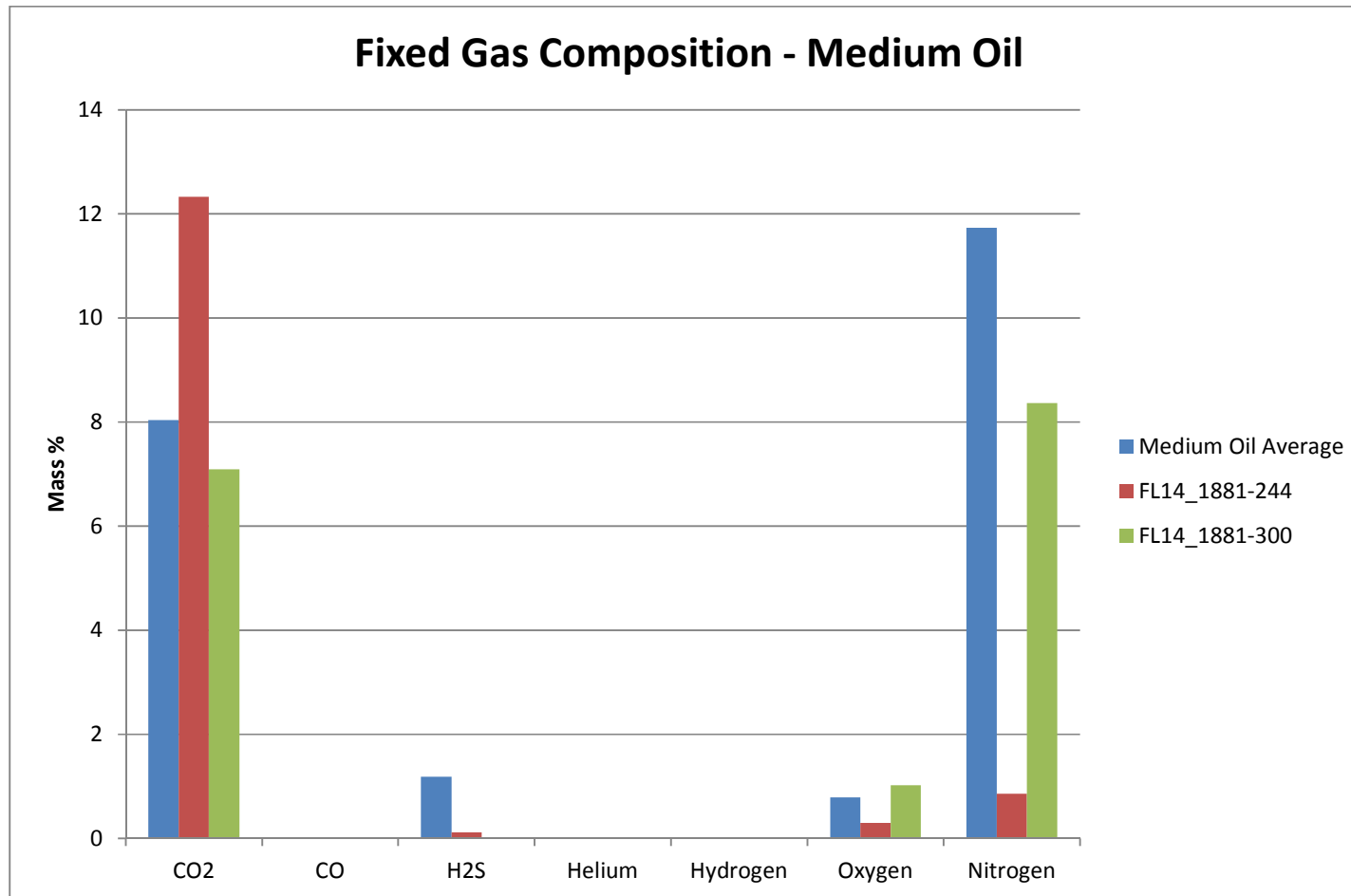


Figure 85: Medium Oil Fixed Gas Composition

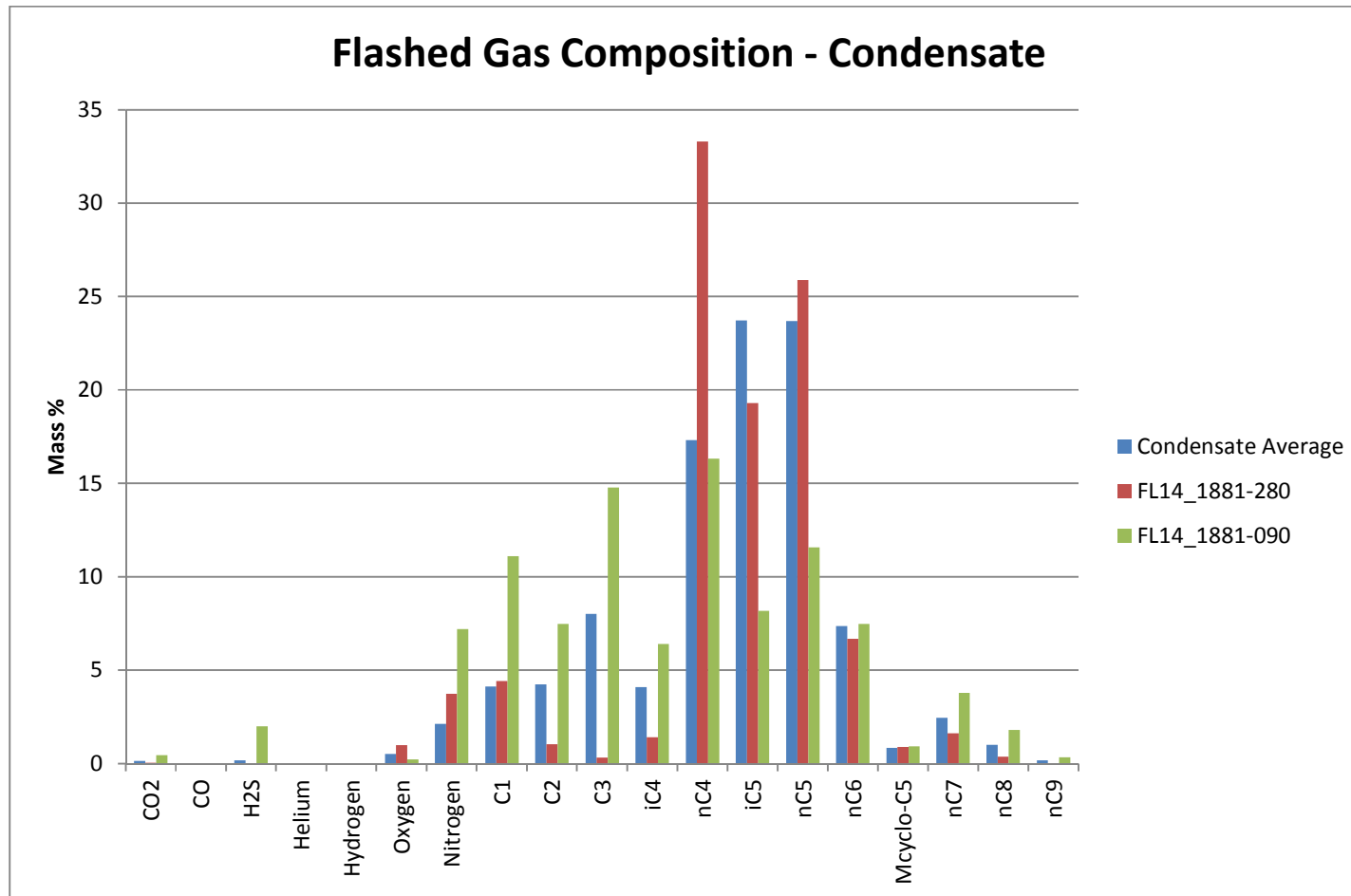


Figure 86: Condensate Flashed Gas Composition



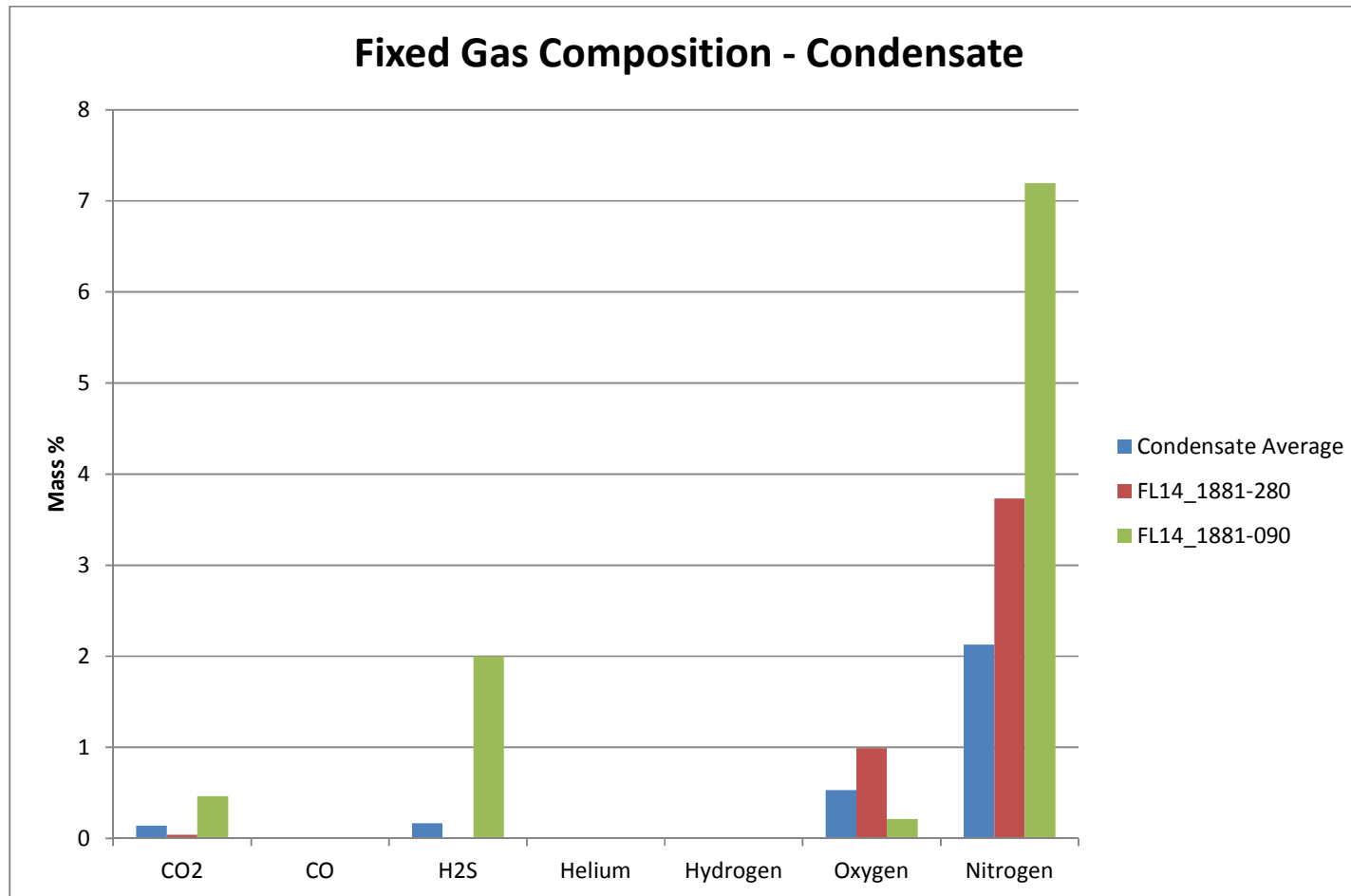


Figure 87: Condensate Fixed Gas Composition

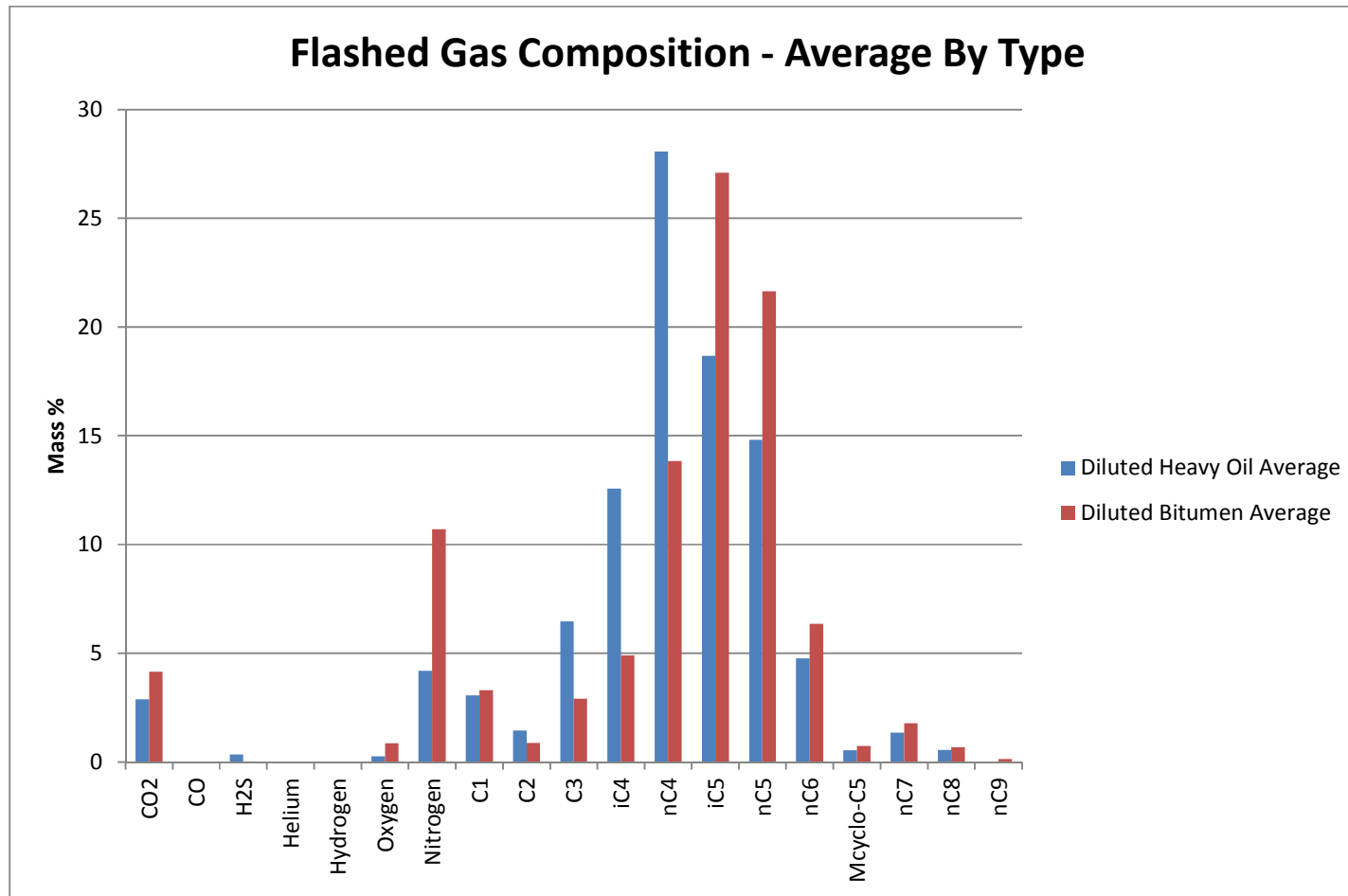


Figure 88: Diluted Heavy Oil and Diluted Bitumen Flashed Gas Composition

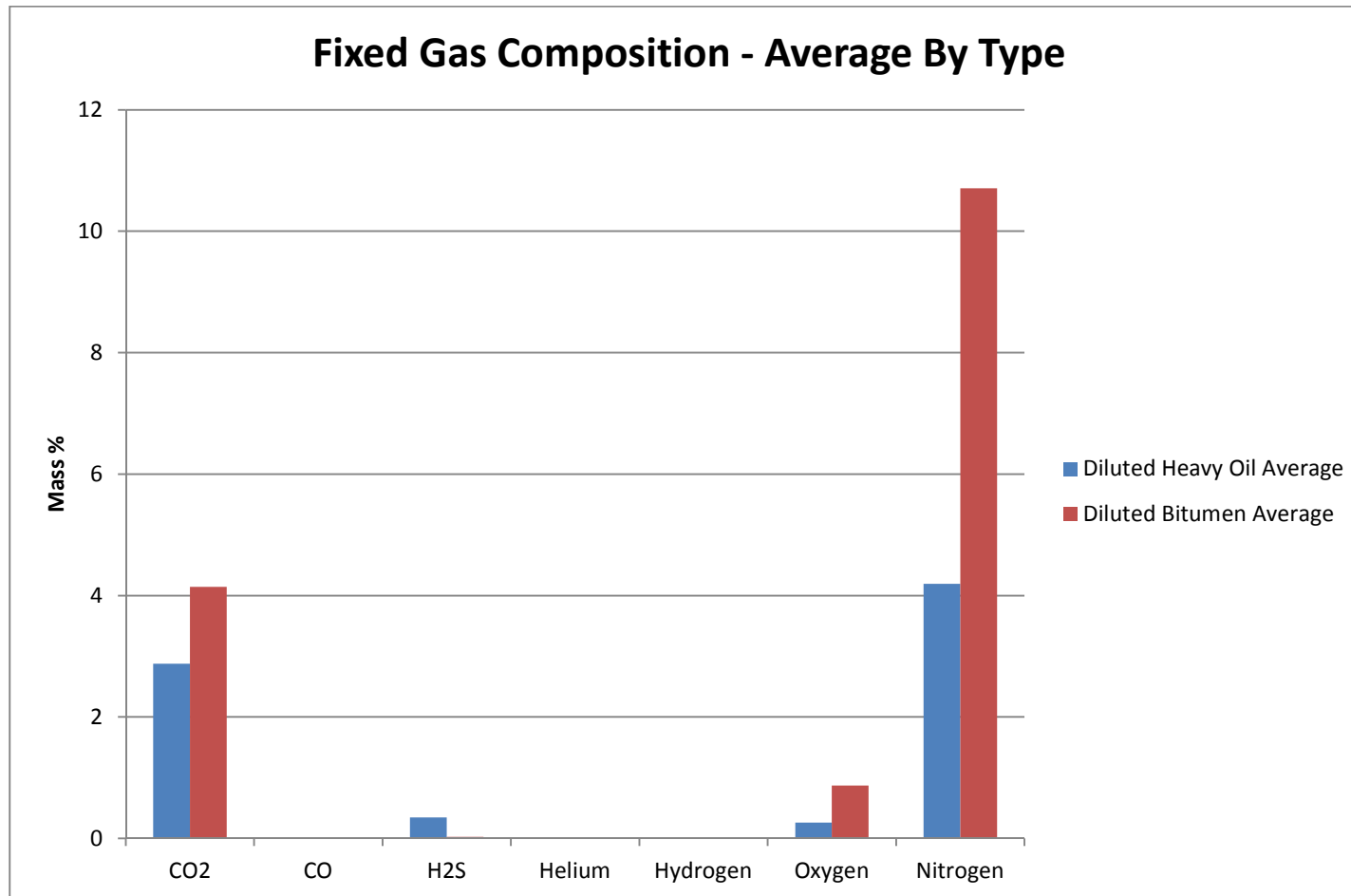


Figure 89: Diluted Heavy Oil and Diluted Bitumen Fixed Gas Composition

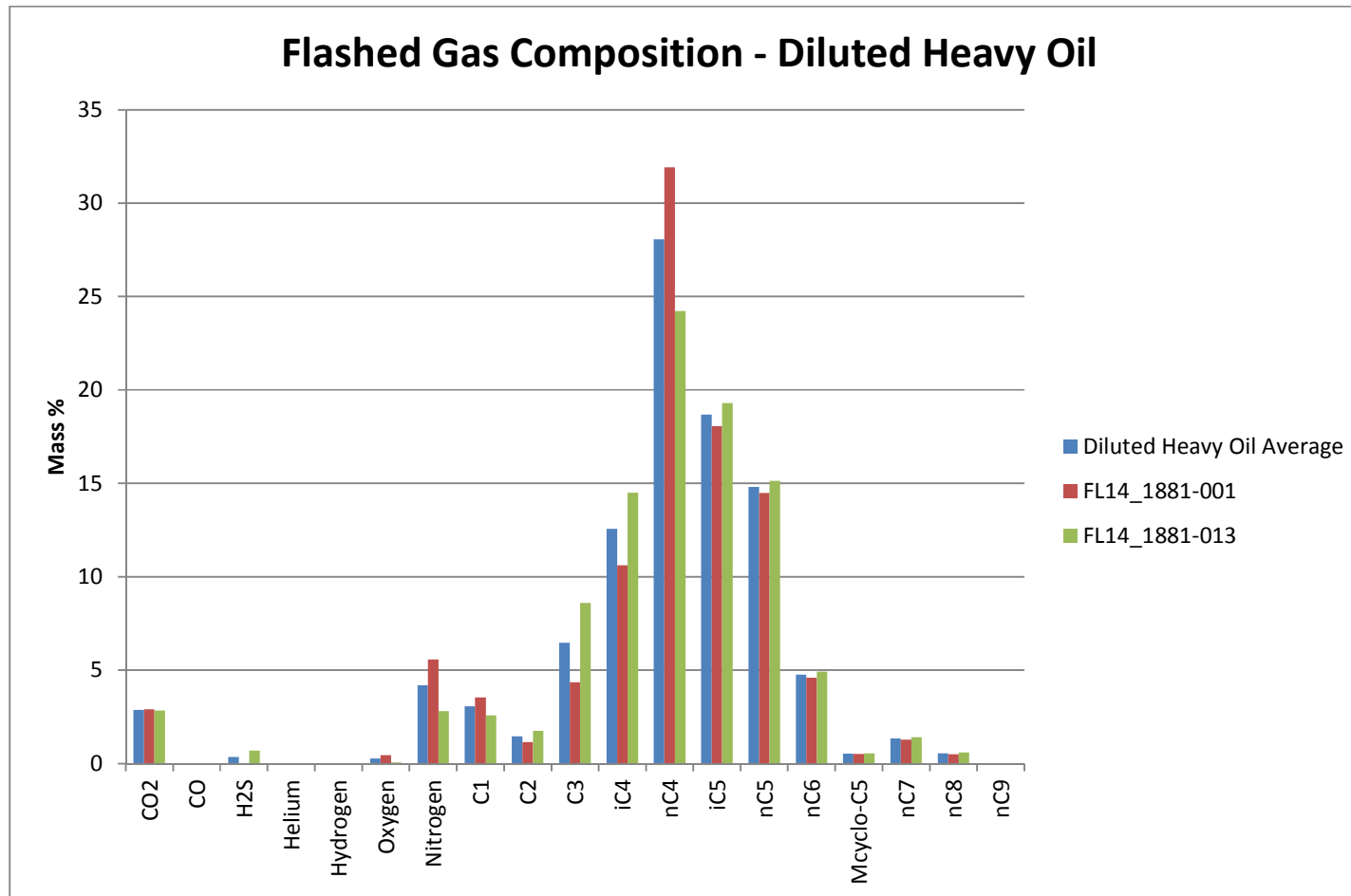


Figure 90: Diluted Heavy Oil Flashed Gas Composition

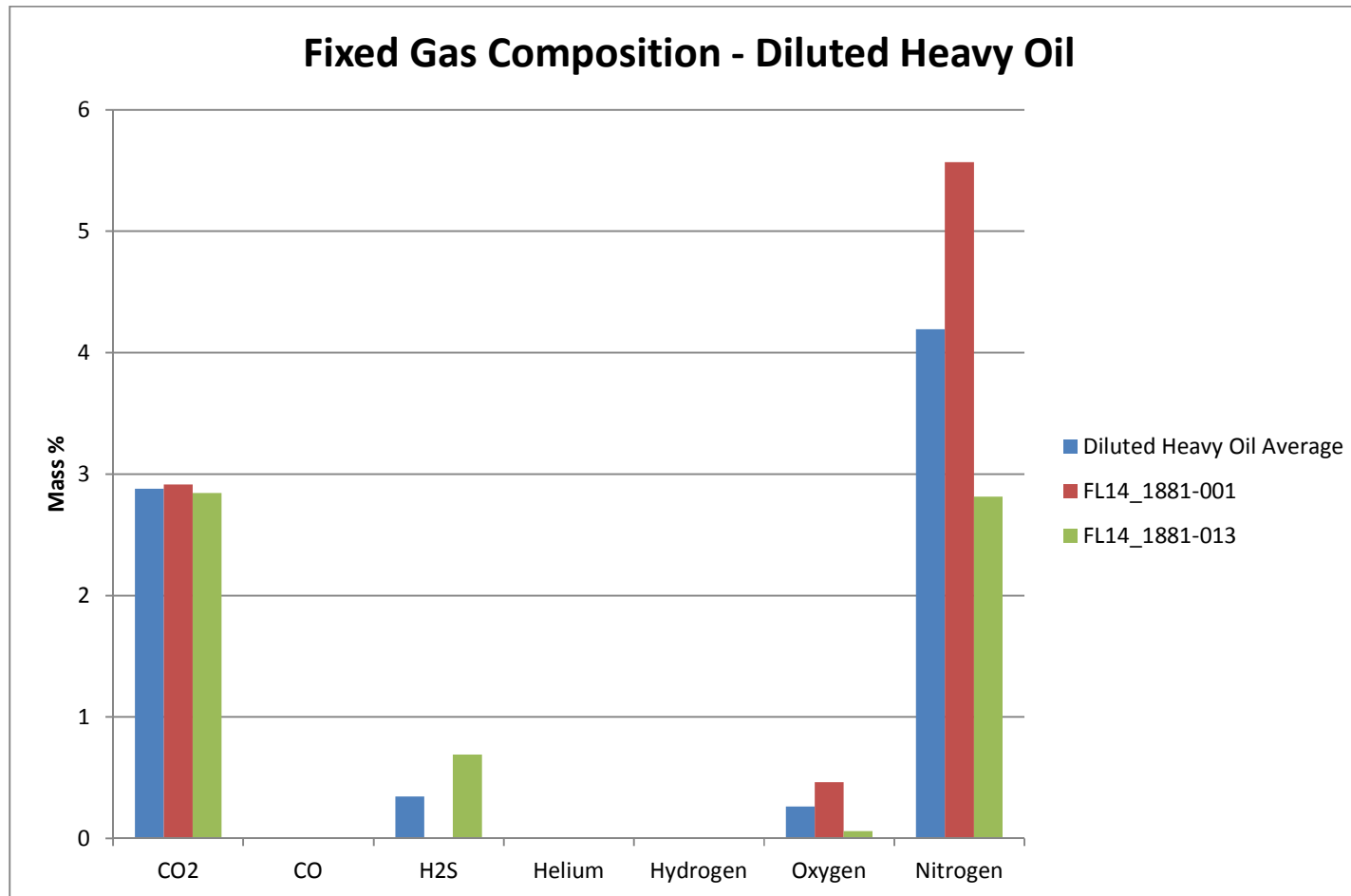


Figure 91: Diluted Heavy Oil Fixed Gas Composition

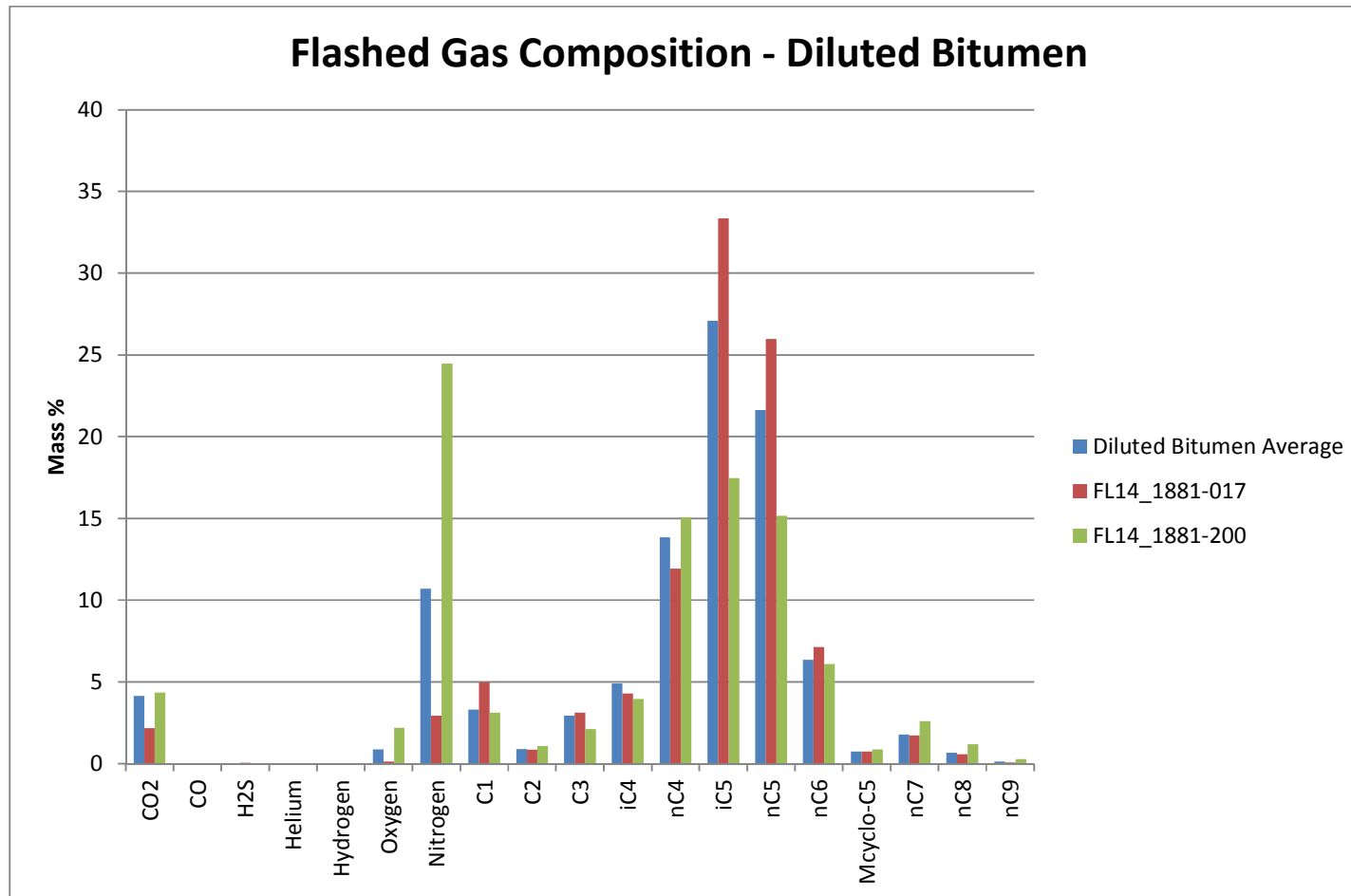


Figure 92: Diluted Bitumen Flashed Gas Composition

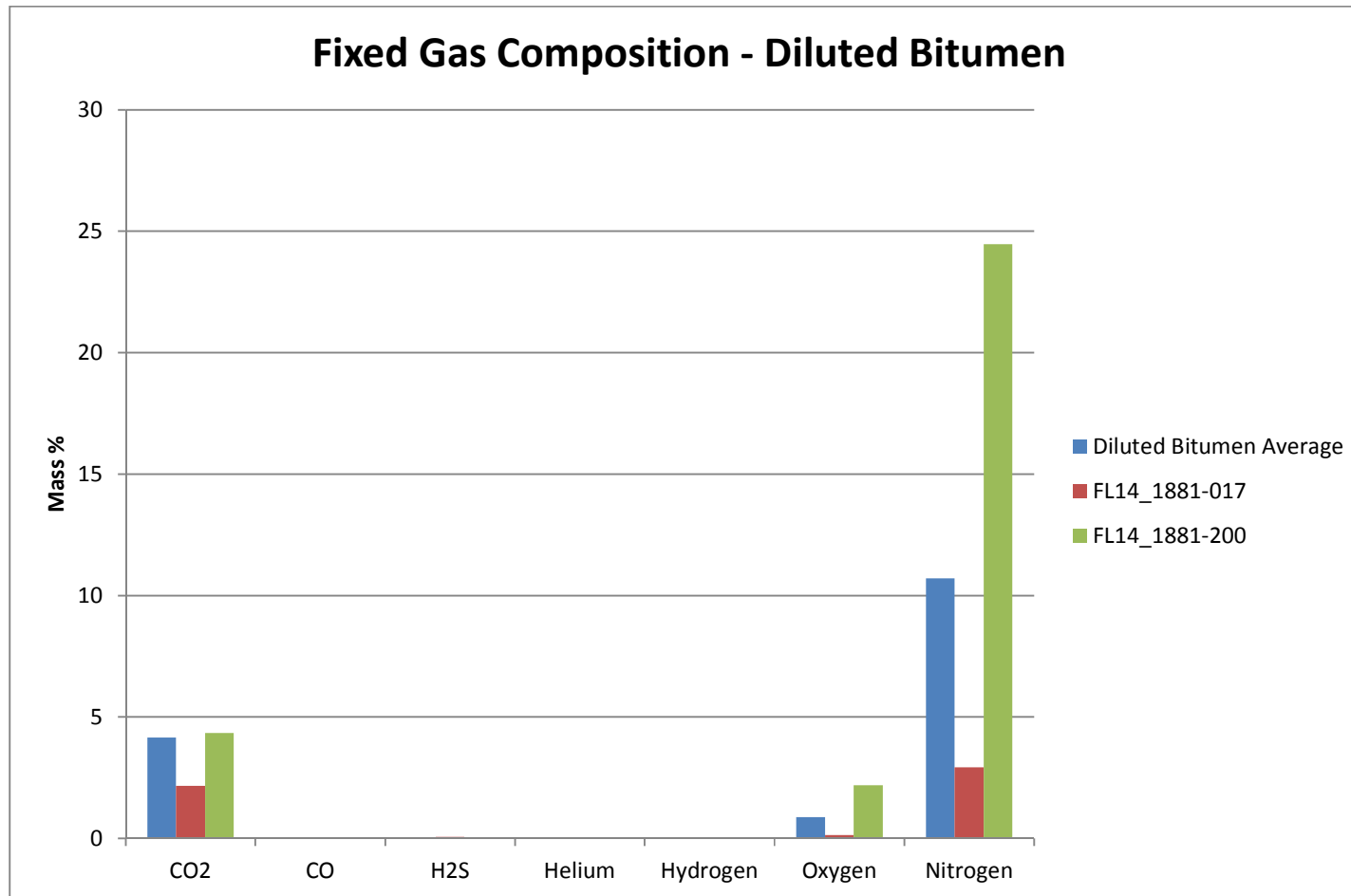


Figure 93: Diluted Bitumen Fixed Gas Composition

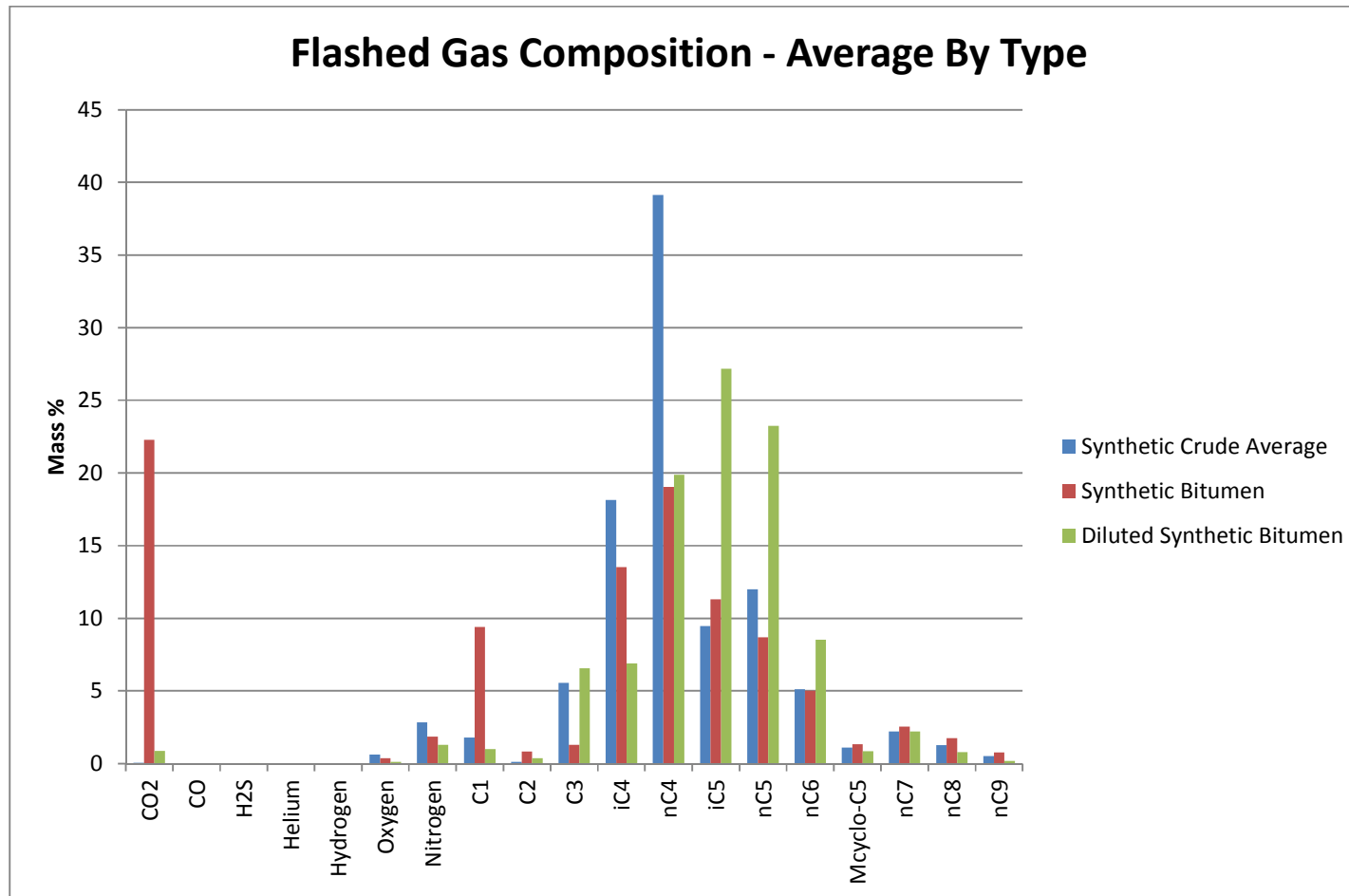


Figure 94: Synthetic Crude, Synthetic Bitumen and Diluted Synthetic Bitumen Flashed Gas Composition



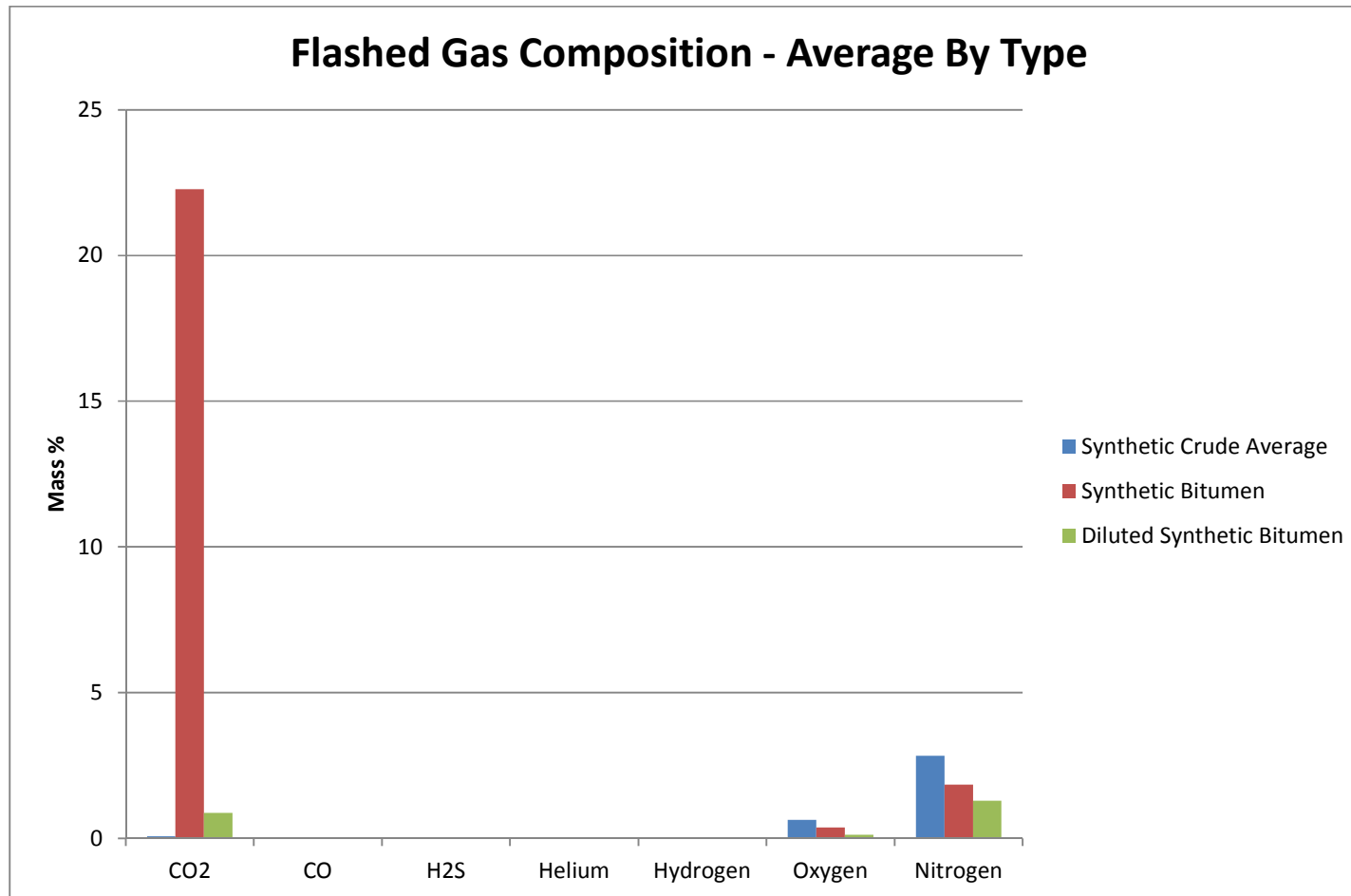


Figure 95: Synthetic Crude, Synthetic Bitumen and Diluted Synthetic Bitumen Fixed Gas Composition

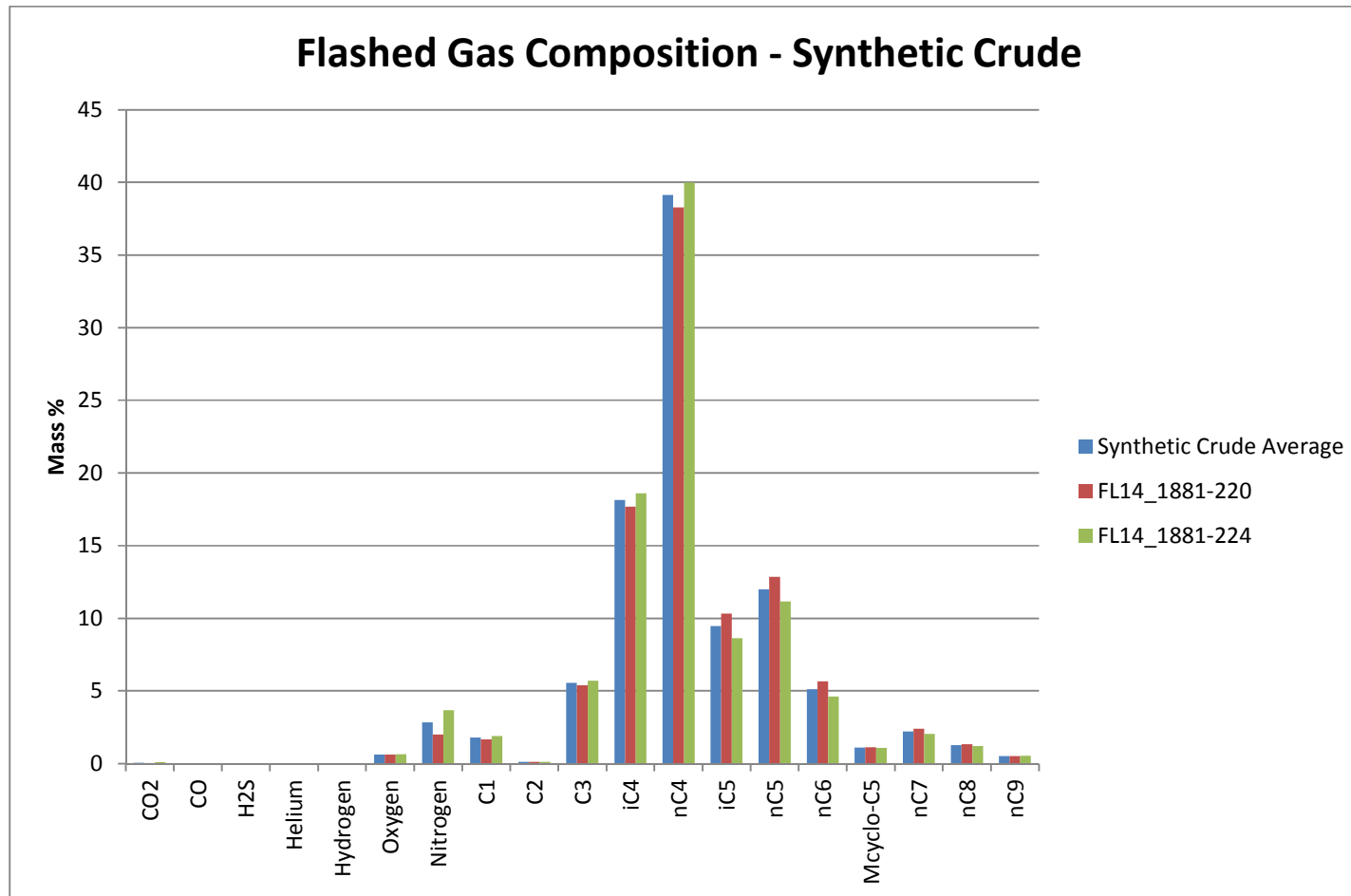


Figure 96: Synthetic Crude Flashed Gas Composition

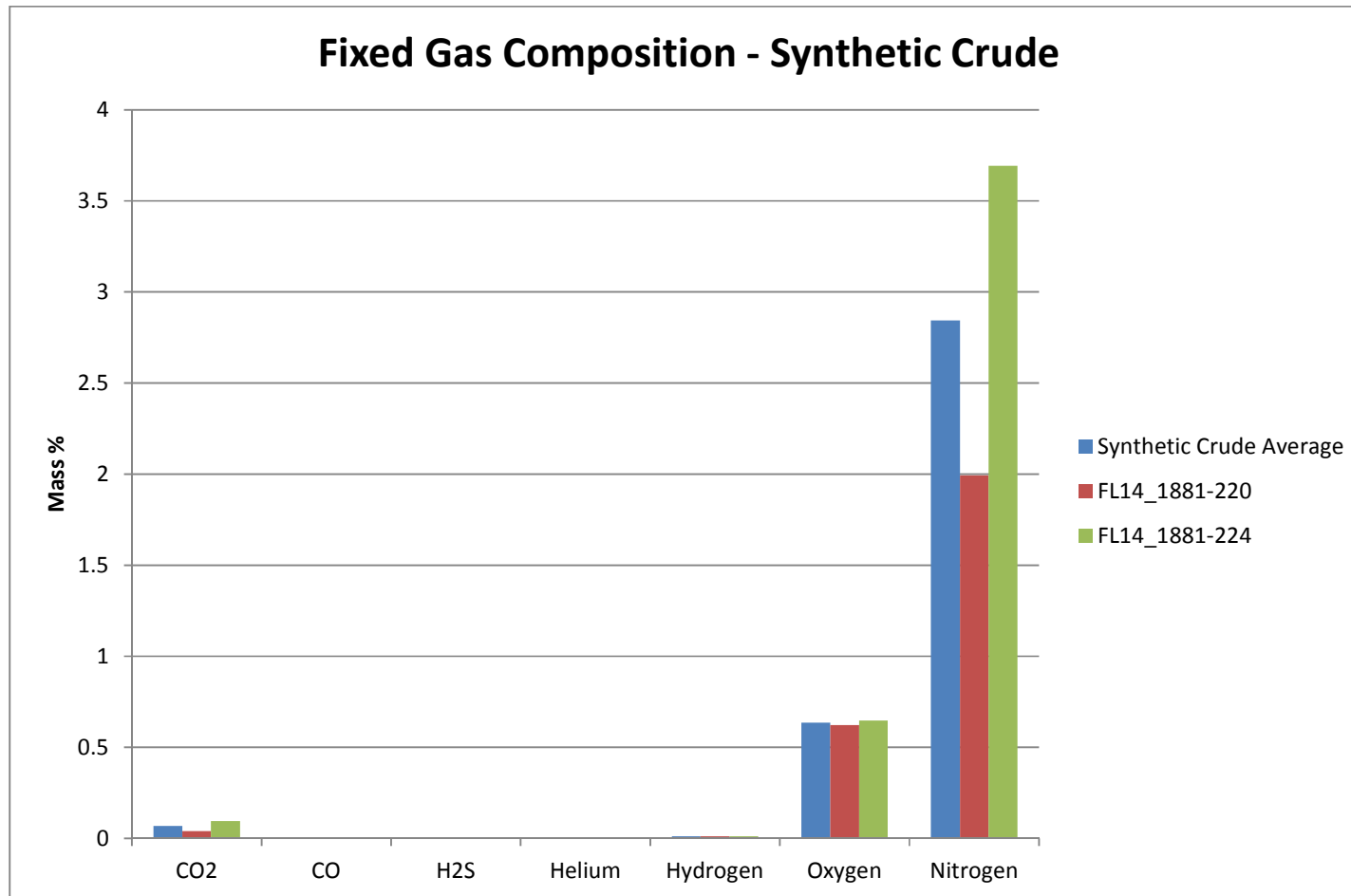


Figure 97: Synthetic Crude Fixed Gas Composition

---

## 8.10 Assessment of Dangerous Goods Regulations

### 8.10.1 Toxic Inhalation Hazard

The results of ASTM D5705 indicate that H<sub>2</sub>S is present in the vapour phase of oils and may pose a toxic inhalation risk. Nine of the samples tested had concentrations of H<sub>2</sub>S at 12,500ppm to 65,000ppm.

The misconception regarding the terms sweet and sour has the potential to cause confusion regarding the toxic inhalation hazard of crude oil and could lead to underestimation of the hazard. Some sweet oils contained high concentrations of H<sub>2</sub>S in the vapour phase and some sour oils contained low concentrations of H<sub>2</sub>S in the vapour phase. That being said, eight out of the nine samples with the highest concentrations of H<sub>2</sub>S in the vapour phase were sour samples.

The caveat when reading the results of ASTM D5705 is that H<sub>2</sub>S concentration in the vapour phase varies as a function of headspace volume, temperature, agitation and the presence of scavengers and the value obtained by this test may not be representative of the concentration of H<sub>2</sub>S in the vapour space of a rail car or truck tank. An example of this was observed at a rail terminal which loads bitumen and synbit. The concentration of H<sub>2</sub>S in the vapour phase above the bitumen as determined by ASTM D5705 at 60°C was 40ppm. However, the bitumen is loaded onto rail cars at 90°C so the concentration during loading is likely greater than 40ppm. In fact, the operators' H<sub>2</sub>S monitors will alarm (threshold = 10ppm) during loading and the procedure is to keep a safe distance during loading. The H<sub>2</sub>S monitors would not alarm during loading of synbit, yet the H<sub>2</sub>S concentration in the vapour phase as determined by ASTM D5705 at 60°C was 2000ppm.

One observation of concern is that bitumen is not regulated as dangerous goods yet a toxic inhalation hazard clearly exists under transportation conditions and is recognized by the producer, as demonstrated in the MSDS provided. Section 3 of the MSDS, Composition/Information on Ingredients, states "Hydrogen sulphide gas may be released upon heating and/or mechanical agitation". Section 15, Regulatory Information, lists the WHMIS classification of bitumen as Class D – Division 2A, 2B: Poisonous and Infectious Material – Materials causing other toxic effects (A: Very toxic material, B: Toxic material).

As previously discussed, there are a number of issues regarding ASTM D5705 such as volatility of H<sub>2</sub>S, applicability of the method, modifications to the method and inability to make correlations to transport conditions. However, ASTM D5705 does provide a measure of H<sub>2</sub>S present in the vapour phase and if the method was performed in a consistent manner using

conditions of headspace and temperature encountered in transport, the results could be used as an indication of the level of risk until such time when a more suitable method is developed.

### 8.10.2 Flammable Liquids

Under Part 2 of the TDG regulations, flammable liquids are assigned a packing group based on their flash point and initial boiling point as shown below in Table 20; with packing group I considered the most flammable and the degree of danger the highest.

**Table 20: Packing Group Classifications of Class 3 Flammable Liquids**

Packing Group	Flashpoint (closed-cup)	Initial Boiling Point
<b>I</b>	-	$\leq 35^{\circ}\text{C}$
<b>II</b>	$<23^{\circ}\text{C}$	$>35^{\circ}\text{C}$
<b>III</b>	$\geq 23^{\circ}\text{C}, \leq 60^{\circ}\text{C}$	$>35^{\circ}\text{C}$

The method most commonly used to determine the IBP is ASTM D86 using a sample collected under atmospheric conditions. However, as demonstrated by the test results, the IBP of the same sample determined by ASTM D86 is consistently higher than the IBP determined by GC analysis of a pressurized sample. The difference in the IBP between methods is large enough that the assignment of the packing group may change based on the method chosen. Table 21 shows the assignment of packing groups for the samples with the highest percentage of light ends based on flash point and method of determining IBP. The samples for which the packing group assignment changed are highlighted in orange. It is interesting to note that the packing group of gasoline would change from II to I if the IBP were determined by GC.

Classification of an oil as packing group I or II may not affect the selection of transport container however there are implications for handling and emergency response. Misclassification could result in improper handling and the development of inadequate safety and security plans and the communication of inaccurate information to emergency responders (CAPP, 2014).

# ANNEX B - AITF REPORT (EN)



**Table 21: Packing Group Classifications Based on Method of Determining IBP**

LIMs #	Flash Point, Closed Cup (°C)	IBP (°C), ASTM D86	Packing Group	IBP (°C), GC Merge	Packing Group
FL14_1881-003	<-30.0	30.9	I	-0.6	I
FL14_1881-007	<-30.0	29.7	I	-0.6	I
FL14_1881-019	<-30.0	30.7	I	-0.6	I
FL14_1881-027	<-30.0	29.4	I	-0.6	I
FL14_1881-051	<-30.0	48.8	II	-0.6	I
FL14_1881-059	<-30.0	44.4	II	-0.6	I
FL14_1881-071	<-30.0	28.1	I	-11.7	I
FL14_1881-075	<-30.0	28.4	I	-0.6	I
FL14_1881-108	<-30.0	32.3	I	-11.7	I
FL14_1881-112	<-30.0	36.1	II	27.8	I
FL14_1881-116	<-30.0	27.6	I	-11.7	I
FL14_1881-120	<-30.0	26.6	I	-11.7	I
FL14_1881-124	<-30.0	33	I	-42.2	I
FL14_1881-128	<-30.0	30.8	I	-0.6	I
FL14_1881-140	<-30.0	36.6	II	-42.2	I
FL14_1881-144	22	92.8	II	62.4	II
FL14_1881-148	-30	33.6	I	-42.2	I
FL14_1881-152	<-30.0	28.5	I	-42.2	I
FL14_1881-168	<-30.0	30.3	I	-42.2	I
FL14_1881-172	<-30	30.7	I	-42.2	I
FL14_1881-176	<-30	34.5	I	-42.2	I
FL14_1881-180	<-30	28.2	I	-42.2	I
FL14_1881-193	<-30	31.4	I	-0.6	I
FL14_1881-201	<-30	39.8	II	-0.6	I
FL14_1881-221	<-30	36.4	II	-0.6	I
FL14_1881-225	<-30	35.2	II	-0.6	I
FL14_1881-229	<-30	28.1	I	-0.6	I
FL14_1881-233	<-30	52.8	II	-0.6	I
FL14_1881-241	<-30	45.7	II	-0.6	I
FL14_1881-281	<-30	23.9	I	-0.6	I
FL14_1881-285	<-30	25.2	I	-11.7	I
FL14_1881-293	<-30	44.7	II	-0.6	I

### 8.10.3 Gases, Class 2

A gas is defined under Part 1 of the TDG regulations as a substance that at 50°C has a vapour pressure greater than 300 kPa or that is completely gaseous at 20°C at an absolute pressure of 101.3 kPa and that is:

- a) compressed (other than in solution) so that when it is packaged under pressure for transport it remains entirely gaseous at 20°C;
- b) liquefied so that when it is packaged for transport it is partially liquid at 20°C;
- c) refrigerated so that when it is packaged for transport it is made partially liquid because of its low temperature; or
- d) in solution so that when it is packaged for transport it is dissolved in a solvent.

Given the vapour pressure results, assignment of subsidiary hazard classification of Class 2 may not be justified for most crude oils, but two samples out of sixty-eight did have a vapour pressure greater than 300 kPa as measured by ASTM D6377. Sample FL14\_1881-244, a medium oil, had a vapour pressure of 527.9 kPa. This sample had the highest percentage of CO<sub>2</sub> and methane (C1) of all the samples at 0.071% and 0.290% respectively. However, this sample was not collected at the point closest to transportation so it is not likely representative of what is transported. Sample FL14\_1881-178, a light oil, had a vapour pressure of 300.8 kPa. This sample had the highest percentage of propane (C3) of all the samples at 2.34%. The high vapour pressure in the case may have been due to ambient sampling temperature and treater operating temperature. This sample is transported by truck, which raises concerns about possible vapour pressure buildup and fugitive emissions. The ability to measure vapour pressure in the field would give operators the opportunity to alter conditions at the battery to reduce vapour pressure prior to transport.

### 8.10.4 Flammable Gases, Class 2.1

Even though most of the samples may not be classified as gases as defined in Part 1 of the TDG Regulations, they do produce flammable vapours as demonstrated by the flash point results.

Flammable gases, Class 2.1, are defined under Part 2 of the TDG regulations as gases that, at 20°C and an absolute pressure of 101.3 kPa:

- a) are ignitable when in a mixture of 13% or less by volume with air, or
- b) have a flammability range with air of at least 12 percentage points determined in accordance with tests or calculations in ISO 10156.

---

The calculations in ISO 10156 were applied to the GOR flashed gas composition to determine if the vapour phase above a crude oil sample was flammable. Since the GOR flashes were done at atmospheric pressure and ambient laboratory temperature (23°C), the evolved gas composition from the GOR analysis is what would be in the vapour phase above that sample of crude oil under atmospheric pressure and equivalent temperature.

According to the ISO 10156 calculations, the pure flashed gas (100% in air) of all samples except one was flammable. This correlates with the flash point results in that all samples produced a flash, so the vapour is in fact flammable. The flashed gas that was not flammable was sample FL14\_1881-142. This is a medium oil from the Birdtail formation in Manitoba. This sample had a flash point of 22°C, an IBP as determined by GC analysis of 62.4°C and the percentage of the sample from C1 to C9 was less than 10% according to the C1 to C24 composition. Due to these factors, the amount of flammable gases in the vapour phase would be very small at the GOR conditions.

To determine whether the vapour phase had a flammability range with air of at least 12 percentage points, the minimum percentage of flashed gas that when mixed with air is flammable was calculated. A concentration of 1% flashed gas in air was used as the starting point and the concentration was increased in 1% steps until the calculations showed that the gas was flammable. The average minimum percentage of flashed gas required to produce a flammable gas is shown below in Figure 98 and the range of percentage of flashed gas required to produce a flammable gas by crude oil type are shown in Figure 99.



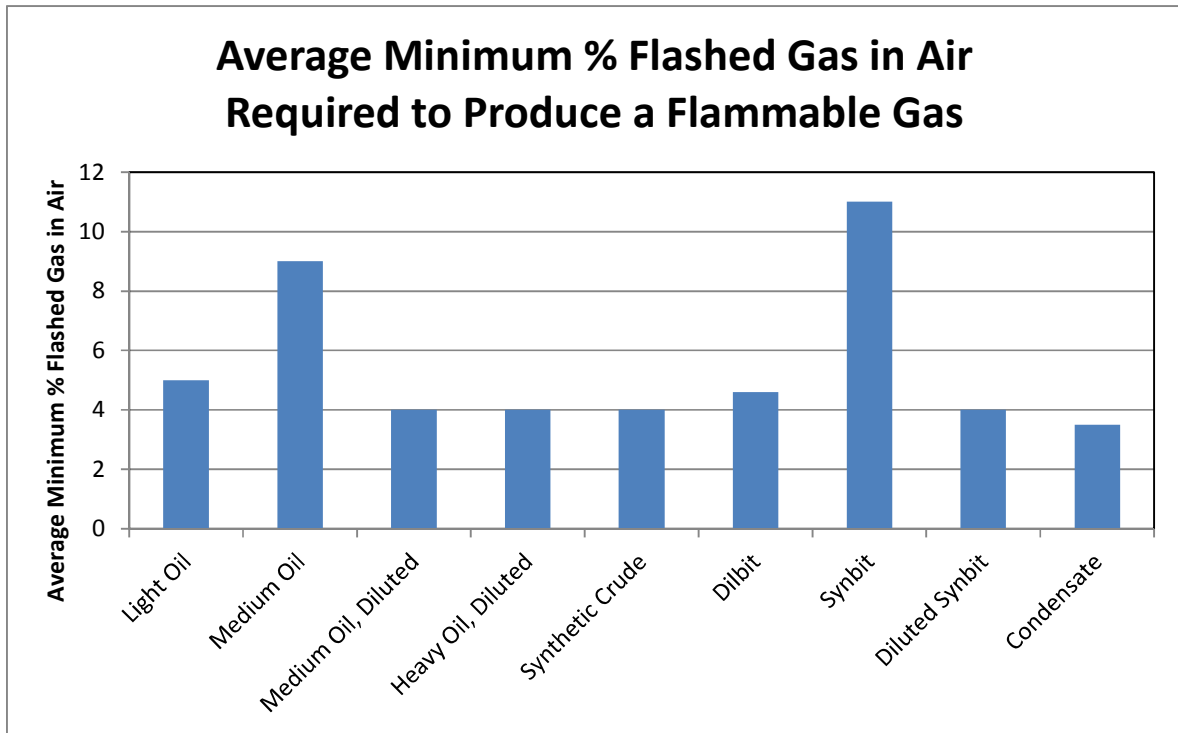


Figure 98: Average Minimum % Flashed Gas in Air Required to Produce a Flammable Gas

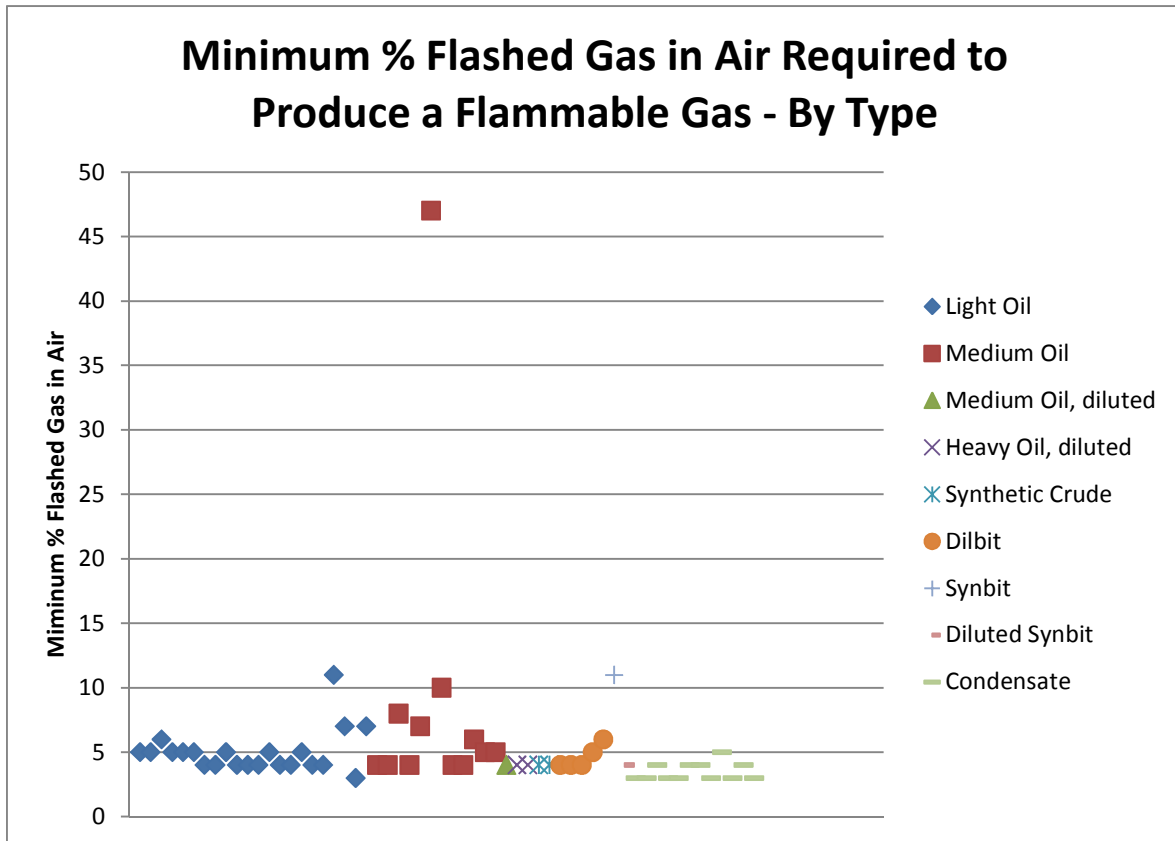


Figure 99: Minimum % Flashed Gas in Air Required to Produce a Flammable Gas – By Type

The variation in minimum percentage of flashed gas required to produce a flammable gas within the crude types as seen in Figure 101 is due to differences in the light end and fixed gas composition of the flashed gas. Sample FL14\_1881-268 required a minimum of 47% flashed gas in air to produce a flammable gas. The flashed gas of this sample contained ~17 mass % CO<sub>2</sub> and 38% N<sub>2</sub>, which are inert gases. As a result, a high concentration of flashed gas in air is required to produce a flammable gas. Samples FL14\_1881-204 (light oil), -272 (medium oil) and -237 (condensate) required the next highest percentage of flashed gas in air to produce a flammable gas. These samples also contained high amounts of CO<sub>2</sub> and N<sub>2</sub>; however the concentration of flammable gases in these samples was higher.

The flashed gas of all of the samples tested (other than FL14\_1881-142) can be classified as a flammable gas according to ISO 10156 and Part 2 of the TDG regulations. However, the ISO 10156 test and calculation methods only determine whether a gas or gas mixture is flammable in

air, they do not cover the determination of flammability limits or flammability ranges of gaseous mixtures (ISO, 2010). Factors such as V/L ratio and temperature that are critical to the composition and amount of vapour produced are not taken into account using ISO 10156.

The method also gives no indication as to whether it is applicable to samples such as crude oil that have a vapour phase but do not meet the definition of a gas as per TDG Part 1. When using ISO 10156 to assess the flammability there is no context given to the samples in terms of the amount of flashed gas produced. The flashed gas from a condensate and a diluted heavy oil may both be flammable but the condensate will produce a greater amount of flashed gas resulting in a greater hazard.

Future work on the flammability of crude oil vapours should be focused on determining the vapour phase composition under specific headspace volumes and temperatures either through equation of state modeling or laboratory experiments, and using those values to determine the upper and lower flammability limits.

## 9 Results and Discussion: Produced Water Samples

### 9.1 Hydrocarbon Content

The amount of hydrocarbon in each produced water sample was determined by ASTM D7678, Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy. TPH in this method refers to hydrocarbons extractable with cyclohexane and measured by infrared (IR) absorption in the region of  $1370 - 1380 \text{ cm}^{-1}$  (7.25 - 7.30 microns). Sample FL14\_1881-084 had a visible layer of hydrocarbon present. The heights of the hydrocarbon and water layers were measured and the amount of hydrocarbon was reported in ppm. Some emulsion was present at the interface and was accounted for as hydrocarbons. The results are shown in Table 22.

Table 22: Hydrocarbon Content of Produced Water Samples

LIMs #	Region	Total Petroleum Hydrocarbons in Water (ppm), ASTM D7678
FL14_1881-080	B.C.	91.8
FL14_1881-084	B.C.	54000
FL14_1881-088	B.C.	115.7
FL14_1881-182	SK	29.9
FL14_1881-185	MB	305.9
FL14_1881-188	MB	1075.6
FL14_1881-213	AB	31.2
FL14_1881-217	AB	76.7
FL14_1881-261	AB	23.3
FL14_1881-265	AB	159.4

### 9.1.1 Composition of the Hydrocarbon Layer

The hydrocarbon layer of sample FL14\_1881-084 was sub-sampled for GC analysis by ASTM D7169. The IBP was determined to be <math>36^{\circ}\text{C}</math>. As the cut off temperature between packing group I and packing group II is  $35^{\circ}\text{C}</math>, use of ASTM D7169 alone cannot be used to assign a packing group since it results in unreliable quantitative analysis of the boiling distribution in the C4-C8 region. The IBP would have to be determined using the GC merge method. This would require collecting a large enough sample to ensure that the volume of the hydrocarbon layer is sufficient for both GC analyses. The volume required for HPLIS-GC and ASTM D7169 is a total of 15mL. The GC-merge method could not be performed on this sample as the volume of the hydrocarbon was insufficient for both GC analyses. Sample FL14_1881-084 and the ASTM D7169 chromatogram are shown in Figures 100 and 101.$

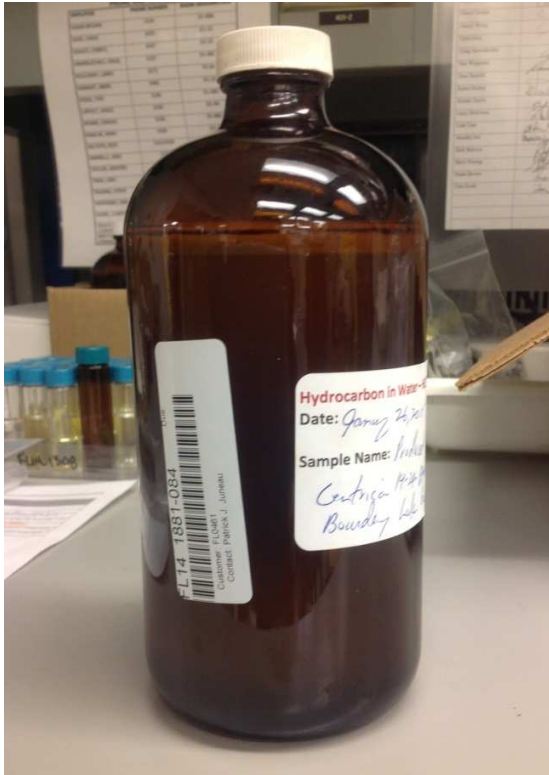


Figure 100: Produced Water Sample FL14\_1881-084

# ANNEX B - AITF REPORT (EN)

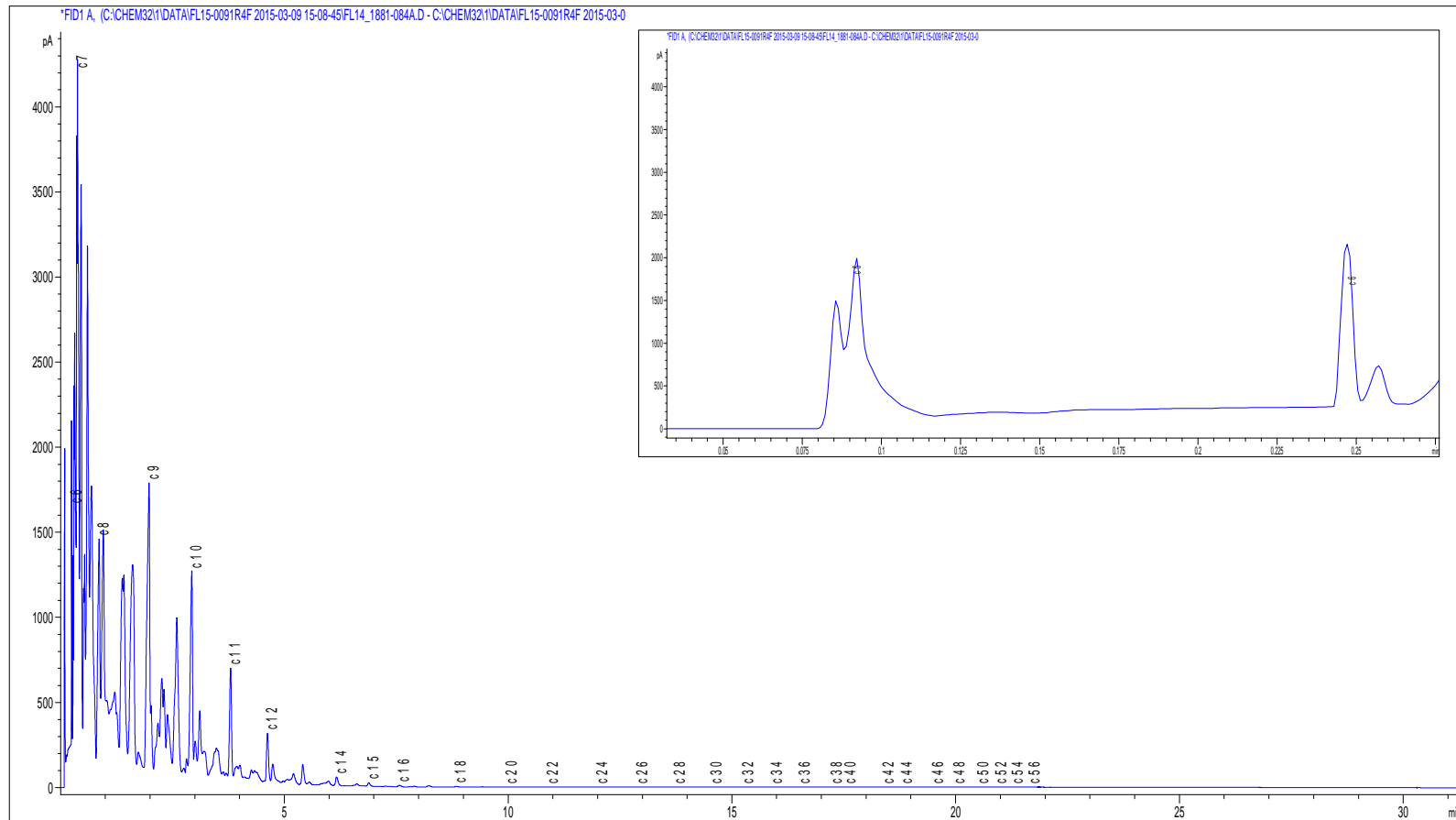


Figure 101: ASTM D7169 Chromatogram of the FL14\_1881-084 Hydrocarbon Layer

## 9.2 Flash Point

The flash point of the produced water samples was determined using ASTM D93 Procedure A, Flash Point by Pensky-Martens Closed Cup Tester.

**Table 23: Flash Point of Produced Water Samples**

LIMs #	Region	Flash Point (°C), ASTM D93 Procedure A
FL14_1881-081	B.C.	52.0
FL14_1881-085	B.C.	<5.0
FL14_1881-089	B.C.	50.5
FL14_1881-183	SK	n/a
FL14_1881-186	MB	n/a
FL14_1881-189	MB	n/a
FL14_1881-214	AB	n/a
FL14_1881-218	AB	n/a
FL14_1881-262	AB	n/a
FL14_1881-266	AB	n/a

A flash point was observed in three of the ten produced water samples in the test temperature range of 5-100°C. The amount of hydrocarbon in the produced water was not the determining factor in whether these sample would flash. Samples 185, 188 and 265 had a greater concentration of hydrocarbons than 081 and 089 yet they did not flash.

The type of oil associated with the samples that flashed are all condensates while the type of oil associated with the samples that did not flash are light oils. Two of these produced waters (FL14\_1881-081 and -085) were sampled at gas plants where condensate is associated with the natural gas produced. The other produced water (FL14\_1881-089) was sampled at a facility where pre-producing gas wells have been converted to saline source water wells. Produced water and hydraulic fracturing water returns from other locations are blended with the saline water for use in operations. The flash point of all the associated oils was <-30°C. While the condensates and light oils associated with these water samples have similar percentages of light ends, the condensates have very little C25+ residue. As a result, the fraction of the oil remaining in the produced water after separation from the oil would be lighter in the samples from the condensate sites than the samples from the light oil sites causing those samples to flash.

According to the flash points, the three produced water samples from B.C. would be considered flammable liquids, however to assign a packing group, the initial boiling point would need to be determined. ASTM D86 is not suitable for samples containing water; large amounts of water will cause the sample to bump and smaller amounts of water will form an azeotropic mixture with the oil and the two components will distill together resulting in an inaccurate IBP. The merged GC method (HPLIS or D7900 and ASTM D7169) could be used to determine IBP but would require a sample of produced water large enough to have a sufficient volume of hydrocarbon layer for sub-sampling.

As shown by the results above, some produced water shipments may contain sufficient amounts of crude oil or condensate that would pose a flammability risk however these may not be the best methods to assess the risk. The closed cup flash point methods used in this project are not meant for non-homogenous products such as produced water and as noted above, ASTM D86 is not a suitable method for determining IBP.

In the case of produced water, the bulk of the material is water and will not ignite. However, hydrocarbon vapours can accumulate in the headspace of a tank and these will ignite. A better approach may be to assess the risk posed by the vapour phase in the headspace above a load of produced water. The composition of the hydrocarbon layer of the produced water could be determined by GC and used to assess the composition of the vapour phase and its flammability.

### 9.3 Hydrogen Sulphide in Produced Water

There has been anecdotal evidence of elevated levels of H<sub>2</sub>S in production fluids. However quantitative data regarding the concentration of H<sub>2</sub>S in production fluids is required in order to confirm if indeed produced water may contain high levels of this toxic gas and assess the safety of these fluids, especially during transport.

The concentration of H<sub>2</sub>S in solution was determined using APHA 4500 S2-E, applicable to all types of aqueous samples from drinking water to industrial wastewater. The concentration of H<sub>2</sub>S in the vapour phase was determined using ASTM D5705, Standard Test Method for Measurement of Hydrogen Sulphide in the Vapour Phase Above Residual Fuel Oils. As with crude oils, ASTM D5705 is not applicable to produced water samples. However since there is no standard method to determine the H<sub>2</sub>S in the vapour phase above produced water samples, ASTM D5705 was used as a starting point.



# ANNEX B - AITF REPORT (EN)



Seven of ten samples were submitted for APHA 4500S2-E and seven were submitted for ASTM D5705. Four of the ten samples collected were submitted for both methods. The results for both methods are shown below in Table 24 and Figure 102.

**Table 24: Solution and Vapour Phase H<sub>2</sub>S Content of Produced Water Samples**

Region	LIMS #	H <sub>2</sub> S in Solution (mg/L), APHA 4500	LIMS #	H <sub>2</sub> S in the Vapour Phase (ppm)
B.C.	FL14_1881-078	71.1		
B.C.	FL14_1881-082	32.3		
B.C.	FL14_1881-086	0.097		
SK			FL14_1881-184	50000
MB			FL14_1881-187	4000
MB			FL14_1881-190	65000
AB	FL14_1881-212	285	FL14_1881215	16250
AB	FL14_1881-216	389	FL14_1881219	16250
AB	FL14_1881-260	25	FL14_1881263	0
AB	FL14_1881-264	19.3	FL14_1881267	1600

The results above indicate that H<sub>2</sub>S is present in some produced waters that are being transported. The four sites that show the highest results (078, 082, 212, and 216) were collected from sites where sour crude oil samples were collected. The samples with the lower results were collected from sweet oil sites. The four samples that were submitted for both H<sub>2</sub>S analyses follow a trend in which the samples with low concentrations of H<sub>2</sub>S in solution have low concentrations of H<sub>2</sub>S in the vapour phase and samples with high concentrations of H<sub>2</sub>S in solution have high concentrations of H<sub>2</sub>S in the vapour phase.

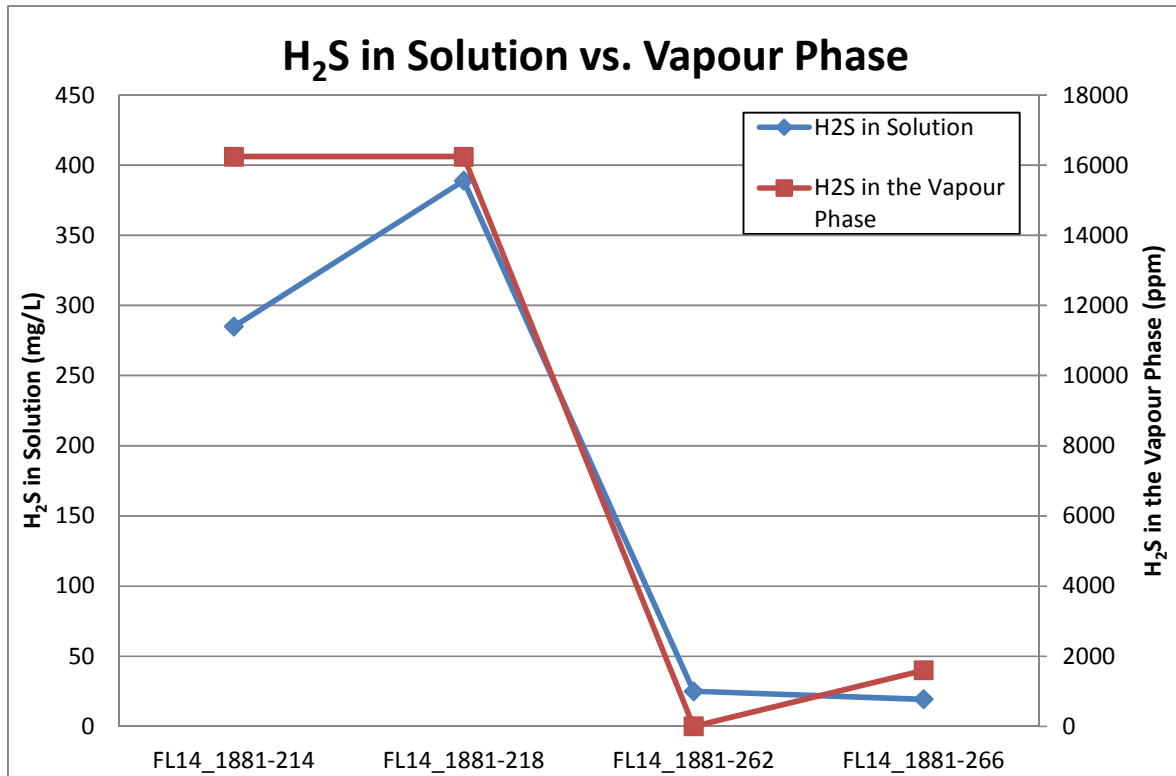


Figure 102: Produced Water H<sub>2</sub>S in Solution vs Vapour Phase

As with the crude oil samples, no general correlation can be established between ASTM D5705 results and actual vapour phase concentrations of H<sub>2</sub>S in storage or transport tanks. Transport Canada may want to consider requiring a designation such as “vapour space may contain hazardous vapours” for produced water that contains H<sub>2</sub>S, along with a warning statement such as “This material may contain or release H<sub>2</sub>S. In a tank or other closed container, the vapor space above this material may accumulate hazardous concentrations of H<sub>2</sub>S”.

#### 9.4 pH

Measurement of the pH of production fluids may provide a means to assess whether additional hazards exist regarding the transportation of produced water. The pH of each produced water sample is shown below in Table 25.

**Table 25: pH of Produced Water Samples**

LIMs #	Region	pH
FL14_1881-081	B.C.	5.95
FL14_1881-085	B.C.	6.70
FL14_1881-089	B.C.	6.63
FL14_1881-183	SK	7.25
FL14_1881-186	MB	6.21
FL14_1881-189	MB	6.35
FL14_1881-214	AB	6.34
FL14_1881-218	AB	6.34
FL14_1881-262	AB	9.16
FL14_1881-266	AB	6.94

The pH of nine of the ten produced waters was slightly acidic and one was slightly basic, with no extremes on either end of the pH scale. Factors that affect the pH of produced water include the amount of dissolved CO<sub>2</sub> and H<sub>2</sub>S and production chemicals. The pH may indicate possible corrosion tendencies of a particular produced water.

---

## 10 Conclusions

### 10.1 Crude Oil

Sixty-eight samples of crude oil destined for transport by rail and/or roadway were collected. Sixty-six were collected across four oil producing regions in Canada; B.C., Alberta, Saskatchewan and Manitoba. The samples were collected from the major oil plays in production in each region and represented a range of crude oil types from condensate to undiluted bitumen. Two samples of natural gasoline condensate from North Dakota which are transported within Canada by truck were also collected.

Testing and analysis of the crude oil samples was focused on the impact of the light ends on the properties of the oils and their role in dangerous goods classification. The results were also used to assess the applicability of current classification requirements under Part 2 of the TDG regulations for Class 3 flammable liquids and Class 2.1 flammable gases, and to determine if there are any additional hazards posed by crude oil that are not currently being considered.

Both pressurized and atmospheric samples were collected at each sampling site. Pressurized samples were collected into floating piston cylinders, which minimize the loss of light ends, and atmospheric samples were collected into 1L glass bottles. FPCs are currently the best containers to collect a single-phase sample however they have some limitations for the low-pressure samples that were collected for this project: FPCs require a skilled operator and a sample source with sufficient pressure to move the piston inside the cylinder. A number of sample sources did not have sufficient pressure and required the use of a pump (Bimba cylinder with check valves) to collect the sample into the FPC. Manual piston sampling cylinders may be better suited for these types of samples; they are lower cost, easier to operate and do not require high sample pressure. These type of cylinders are available but are not yet approved for transport. Sampling procedures using these manual piston cylinders are currently under development at ASTM under work item WK49954.

Density, vapour pressure (V/L 4:1 and 50°C), IBP by ASTM D86 distillation, water content, concentration of H<sub>2</sub>S in the vapour phase and flash point were determined using the atmospheric samples. The vapour pressure (V/L 0.2:1 and 50°C), C1 to C24 composition, IBP by GC-merge, boiling point distribution, GOR and flashed gas composition were determined using the pressurized samples.

The effect of preserving the light ends through pressurized samples is clearly seen in the vapour pressure (V/L 4:1) and IBP measurements. The vapour pressure determined by ASTM D323M

tends to be lower than the vapour pressure determined by ASTM D6377 since components such as C1-C2 and gases such as CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S are lost due to outgassing during sample transfer or the air saturation steps. Since these components can have a significant impact on vapour pressure, ASTM D323M is not a suitable method for determining vapour pressure of live crudes or samples containing light ends and gases such as CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S.

Comparison of the IBP determined by ASTM D86 and GC-merge showed that the ASTM D86 IBP was much higher. The difference in IBP between the two methods ranged from 8°C to 79°C. Based on the results observed, the most accurate method for determining IBP is the GC merge method in which the ASTM D8003 data is merged with the ASTM D7169 data. The IBP is defined as the temperature at which 0.5 mass % has eluted off the column. The technique used for this GC-merge follows guidelines of ASTM D7900 whereby data from a light ends analysis is mathematically combined with simulated distillation data from method ASTM D7169. ASTM D7900 does not allow for injection of pressurized samples. ASTM D8003 allows for the injection of pressurized samples, avoiding the loss of highly volatile components and maintaining sample integrity. The two data sets are then merged at C9 to give a complete boiling point distribution of the whole sample. IBP cannot be determined by ASTM D7169 alone due to the incomplete separation of light ends and CS<sub>2</sub> quenching in the C4 to C8 region and the resulting unreliable quantitative analysis of the boiling distribution in that region. ASTM D86 is not the most accurate method for determining IBP of samples containing light ends due to light end loss that occurs as a result of evaporation during transfer from the sample container to the distillation flask, vapour loss during the distillation and distillation loss of non-condensable light ends at ASTM D86 conditions.

The volatility of crude oil is related to its light ends content as physical properties of crude oils such as vapour pressure and gas/oil ratio (GOR) are impacted by the amount and composition of the light ends. The average vapour pressures (V/L 0.2:1 & 50°C) and GORs of the crude oils followed the pattern expected based on composition. Condensates, with the highest percentage of light ends and the least amount of C25+ residue had the highest average vapour pressure and GOR. Synthetic crude and synthetic bitumen, with the lowest percentage of light ends had the lowest vapour pressures and GOR. All other samples fell in the range between condensate and synthetic crude according to their composition. The effect of diluent on the vapour pressure was shown by the increased vapour pressure and GOR of the diluted samples as compared to the undiluted samples. The vapour pressure and GOR are not just affected by the amount of light ends but also by the composition of the light ends. Hydrocarbons in the range of C1 to C4 have the most significant effect; a small increase in C1 to C4 has a greater effect than an increase in the range of C1 to C6 or C1 to C8.

The presence of H<sub>2</sub>S in crude oil presents a toxic inhalation and flammability hazard during transport as it may accumulate in the vapour phase. However, the use of ASTM D5705 to measure H<sub>2</sub>S in the vapour phase above a crude oil sample is problematic for a number of reasons. The method was not designed for use with crude oils, it is subject to modifications based on the operator or sample type and no general correlation can be established between this field test and actual vapour phase concentrations of H<sub>2</sub>S in storage or transport tanks. Particular attention must be paid to the sample collection and timing of the test. The sample bottles must be filled full and the test must be performed within 4 hours of sampling due to the volatile nature of H<sub>2</sub>S and the potential for loss of H<sub>2</sub>S during storage and handling.

An example of the inconsistency between results at test conditions and results at field conditions was observed at a rail terminal which loads bitumen and synbit. The concentration of H<sub>2</sub>S in the vapour phase was measured using ASTM D5705 at 60°C. However, the bitumen is loaded onto rail cars at 90°C so the concentration during loading is likely greater than ASTM D5705 results would indicate. In fact, the operators' H<sub>2</sub>S monitors will alarm (threshold = 10ppm) during loading and the procedure is to keep a safe distance during loading. The H<sub>2</sub>S monitors would not alarm during loading of synbit, yet the H<sub>2</sub>S concentration in the vapour phase as determined by ASTM D5705 at 60°C was 2000ppm.

It was also observed that bitumen is not regulated as dangerous goods yet a toxic inhalation hazard clearly exists under transportation conditions and is recognized by the producer, as demonstrated in the MSDS provided.

The limitations of ASTM D5705 and the results described above point to a need to develop a method of measuring H<sub>2</sub>S in the vapour phase that is fit for purpose and has the capability of controlling the variables affecting release of H<sub>2</sub>S (sampling method, temperature, V/L ratio and agitation). Ideally, a method of measuring vapour phase H<sub>2</sub>S would set a single bound condition in terms of temperature and headspace. Measuring vapour phase H<sub>2</sub>S using proper sampling techniques, and temperature and headspace conditions in the range normally encountered during operations or transport, would give a better assessment of the risk. Development of a method and knowledge of H<sub>2</sub>S concentrations in the vapour phase would help to inform regulators and provide guidance on setting thresholds for H<sub>2</sub>S. Testing conditions could then be specified in regulations.

The misconception regarding the terms sweet and sour has the potential to cause confusion regarding the toxic inhalation hazard of crude oil and could lead to underestimation of the

hazard. Some sweet oils contained high concentrations of H<sub>2</sub>S in the vapour phase and some sour oils contained low concentrations of H<sub>2</sub>S in the vapour phase.

A conservative approach to the hazard presented by H<sub>2</sub>S would be to require a secondary classification for samples containing a concentration of H<sub>2</sub>S in the vapour phase above a level set by Transport Canada, indicating that the vapour phase could potentially contain toxic amounts of H<sub>2</sub>S.

The assignment of a packing group under Part 2 of the Transportation of Dangerous Goods (TDG) regulations is based on flash point and IBP. As most of the samples had a flash point at or below -30°C, the flash point does not provide a means of differentiating the samples. The only way to differentiate the samples and assign a packing group is by IBP. The method chosen to measure the IBP affected the assignment of a packing group; some samples assigned to packing group II based on the ASTM D86 IBP were re-assigned to packing group I based on the GC merge IBP. Assignment of the correct packing group is critical as it impacts handling and the development of safety and security plans and the communication of information to emergency responders.

Two samples met the definition of a gas as per Part 1 of the TDG regulations: a substance that at 50°C has a vapour pressure greater than 300kPa and that is in solution so that when it is packaged for transport it is dissolved in a solvent. In the case of crude oil, the oil is considered to be the solvent. In one case, the high vapour pressure was due to incorrect sampling point and the sample may not be representative of what is transported. In the other case, the high vapour pressure was due to treater conditions and ambient sampling temperature. The vapour pressure results correspond to the compositional data and GOR results for these samples. Assignment of subsidiary hazard classification of Class 2 may not be justified for most crude oils, however since one sample that is transported by truck did meet the requirement; the possibility should not be ignored. This sample represents 1.5% of all the samples collected and 4% of all light oils. This may seem like a small percentage but if the numbers are representative of what is in transport, this is a concern. The sample is transported by truck, which raises questions about the buildup of vapour pressure in the truck tank and the possibility of fugitive emissions. The ability to measure vapour pressure in the field would give operators the opportunity to alter conditions at the battery to reduce vapour pressure prior to transport.

Whether crude oils are classified as gases or not, they do produce vapours that are flammable. This is evidenced by the fact that all samples produced a flash point. The flashed gas composition of the GOR analysis was used in the ISO 10156 calculations to determine if the

vapour phase was flammable. The pure flashed gas (100% in air) of all samples except one was flammable. Each of these gases also had a flammable range of at least 12 percentage points in air, meeting the definition of a flammable gas Class 2.1, as defined in ISO 10156 and under Part 2 of the TDG regulations. There are some limitations regarding the use of ISO 10156 to assess the flammability of the vapour phase of crude oil samples: the method gives no indication as to whether it is applicable to these type of samples, it does not cover the determination of flammability limits or flammability ranges of gaseous mixtures and there is no context given to the samples in terms of the amount of flashed gas produced. Future work should be focused on determining the vapour phase composition under specific headspace volumes and temperatures and using those values to determine the upper and lower flammability limits. Consideration should also be given to collection samples of the vapour space in truck tanks and rail cars to enable comparison with field data and laboratory data.

There were two gaps identified in the type of samples collected. One was at transloading facilities, where rail cars can be filled either with a single product or a blend of products. The blending of products occurs in the rail car. The only available sampling point was the meter shack in between the truck and the rail car, which meant that only the source oils and not the blend could be sampled. As per the sampling protocol, samples were to be collected at the point closest to the outbound transportation loading point in order to be representative of the product being transported. In this case, the samples taken were similar to, but not the same as, what was actually being transported by the rail car. The other gap in sample collection was emulsions. Crude oil emulsions are frequently shipped over short distances from a wellhead or a battery to another battery where it is cleaned and/or treated. Virtually all of crude oil emulsion transportation is handled by trucks, with a small amount being transported by pipeline.

Another point of consideration for Transport Canada is the accuracy of the MSDS for crude oil being transported. The MSDS is often used as the only source of information for classifying the crude oil and the test data may not be up to date. It is also not clear whether shippers verify the values stated in the MSDS. It would be a good idea for Transport Canada to compare the dangerous goods classification in the MSDS collected for all samples with the test results to identify any discrepancies. To ensure that the MSDS and classification of the crude oils is accurate and current, testing should occur at all points of custody transfer (batteries, truck, rail and transloading facilities) with sufficient frequency. Known products could be tested less frequently (annually or semi-annually) and the testing frequency could be increased if there was a change in product composition due to a new source, blending conditions or seasonality.



## 10.2 Produced Water

Ten produced water samples collected at batteries and gas plants in British Columbia, Alberta and Saskatchewan where a sample of crude oil was also collected. The produced water samples were tested to determine the composition of the water, to assess what hazards may be present and the applicability of current TDG regulations to produced water.

All of the produced water samples contained hydrocarbon as determined by ASTM D7678. The amount of Total Petroleum Hydrocarbons varied from 23 to 54,000ppm. Current TDG regulations define a flammable liquid in terms of flash point and IBP. Given that the samples contained hydrocarbons, there was a possibility that they may flash and could be defined as flammable liquids. Three of the samples did flash using ASTM D93, however this method was not designed for non-homogenous samples such as produced water and it is not known how the presence of the water may affect the flash point. The IBP of the produced water samples could not be determined by ASTM D86 as the method is not suitable for samples containing large amounts of water. The IBP would have to be determined by merged GC method (HPLIS or D7900 and ASTM D7169) which would require a sample large enough to have a sufficient volume of hydrocarbon layer for sub-sampling. Given the unsuitability of the flash point and ASTM D86 methods for these types of samples, the current Class 3 TDG regulations as written may not be applicable to produced water.

The concentration of H<sub>2</sub>S in solution and in the vapour phase of produced water was measured in order to assess the safety of these fluids, especially during transport. ASTM D5705 was used to measure the concentration of H<sub>2</sub>S in the vapour phase. The same issues with the method when used with crude oil also apply to produced water; the method was not designed for the sample type and no general correlation can be established between this field test and actual vapour phase concentrations of H<sub>2</sub>S in storage or transport tanks. The four samples that were submitted for both H<sub>2</sub>S analyses follow a trend in which the samples with low concentrations of H<sub>2</sub>S in solution have low concentrations of H<sub>2</sub>S in the vapour phase and samples with high concentrations of H<sub>2</sub>S in solution have high concentrations of H<sub>2</sub>S in the vapour phase. However since there are only four data points, no extensive conclusions can be drawn.

The main risk posed by hydrocarbons and H<sub>2</sub>S present in produced water is due to the accumulation of these substances in the headspace of a tanker truck, presenting a flammability and/or health risk. Test methods to determine the concentration of H<sub>2</sub>S and hydrocarbons in the vapour phase under transport conditions would be required to assess the risk that may be present. Consideration should also be given to collection samples of the vapour space in truck tanks and rail cars to enable comparison with field data and laboratory data.

As a conservative approach, Transport Canada may want to consider requiring a designation such as “Vapour Space may contain Hazardous and/or Flammable Vapours” for produced water that contains H<sub>2</sub>S and/or hydrocarbons above a level set by Transport Canada, along with applicable warning statements. Statements such as “This material may contain or release H<sub>2</sub>S. In a tank or other closed container, the vapor space above this material may accumulate hazardous concentrations of H<sub>2</sub>S” could be used for H<sub>2</sub>S and “Handle as a flammable liquid. Tank headspaces should always be regarded as potentially flammable and care should be taken to avoid static electrical discharge and all ignition sources during filling, discharging and sampling from storage tanks” could be used for hydrocarbons.

### 10.3 Summary

In summary, the properties of importance to TDG classification of Canadian crude oils and condensates utilizing sealed sample containers and current modern laboratory methods were determined. Samples were representative of all major types of product transported by rail and road. Bitumen, heavy oil, diluted heavy oil, dilbit, synbit, diluted synbit, light and medium oil, and condensates were collected and analyzed. Produced water properties were also determined.

Based on the results, AITF makes the following conclusions and recommendations:

#### Conclusions:

- Sampling procedures using a sealed pressurized system which maintains a single-phase sample eliminates the loss of light ends. Samples obtained in this manner ensured that the resulting laboratory determination was representative of the product.
- Specialized and newly industry developed laboratory procedures utilized in this study ensured that samples were not compromised by fugitive evaporative losses before analysis. The difference in vapor pressure and IBP values compared to traditional analyses from samples collected in traditional sample containers was obvious.
- The most accurate method for determining IBP of live crudes and samples containing light ends is the GC merge method in which the ASTM D8003 data is merged with ASTM D7169 data. The difference in IBP between ASTM D86 and the GC merge method was large enough to affect the assignment of the packing group.
- The properties of vapour pressure and GOR are clearly impacted by both the amount and composition of light ends. As the concentration of light ends increases, both the vapour pressure and GOR increase. Hydrocarbons in the range of C1 to C4 have the greatest impact, the impact decreases with increasing carbon number.

- Although there are issues with using ASTM D5705 to measure the H<sub>2</sub>S in the vapour phase, at this point in time it does provide a measure of H<sub>2</sub>S present in the vapour phase that could be used to assign a subsidiary classification if the method was performed in a consistent manner. A conservative approach would be to require a secondary classification for samples containing a concentration of H<sub>2</sub>S in the vapour phase above a level set by Transport Canada, indicating that the vapour phase could potentially contain toxic amounts of H<sub>2</sub>S.
- Two samples met the definition of a gas as per Part 1 of the TDG regulations; however only one was representative of product that is transported. This sample represented 1.5% of all the samples collected and 4 % all light oils, therefore the possibility of assignment of subsidiary hazard classification of Class 2 should be explored further.
- Crude oils and condensates do produce vapours that are flammable as evidenced by the fact that all samples produced a flash point. The pure flashed gas (100% in air) from the GOR analysis (100% in air) of all samples except one was flammable as per ISO 10156 calculation results. Each of these gases also had a flammable range of at least 12 percentage points in air, meeting the definition of a flammable gas Class 2.1, as defined in ISO 10156 and under Part 2 of the TDG regulations.
- There are some limitations regarding the use of ISO 10156: the method gives no indication as to whether it is applicable to the vapour phase above crude oil, it does not cover the determination of flammability limits or flammability ranges of gaseous mixtures and there is no context given to the samples in terms of the amount of flashed gas produced.
- Current Class 3 TDG regulations as written may not be applicable to produced water given the unsuitability of the methods used to determine flash point and IBP.
- The presence of H<sub>2</sub>S was confirmed in all produced water samples tested.
- Samples submitted for the determination of H<sub>2</sub>S in solution and in the vapour phase follow a trend in which the samples with low concentrations of H<sub>2</sub>S in solution have low concentrations of H<sub>2</sub>S in the vapour phase and samples with high concentrations of H<sub>2</sub>S in solution have high concentrations of H<sub>2</sub>S in the vapour phase. However since there are only four data points, no extensive conclusions could be drawn.
- The main risk posed by hydrocarbons and H<sub>2</sub>S present in produced water is due to the accumulation of these substances in the headspace of a tanker truck, presenting a flammability and/or health risk.

---

## Recommendations

- Conduct a sampling campaign during the summer/fall to determine seasonality differences in crude oil and condensate composition. Factors such as ambient temperature at the time of sampling, processing conditions at the batteries and pipeline specifications may affect the light end content and total composition of the samples.
- Future sampling campaigns should include collection of two additional sample types identified:
  - Blends from rail tank cars at transloading facilities where blending occurs in the rail car and verification of the MSDS used for these blends.
  - Emulsions of crude oil and water. Crude oil emulsions are frequently shipped over short distances from a wellhead or a battery to another battery where it is cleaned and/or treated and virtually all of crude oil emulsion transportation is handled by trucks,
- The ability to measure vapour pressure in the field using standardized equipment and methods would give operators the opportunity to alter conditions at the battery to reduce vapour pressure prior to transport.
- There is a need to develop a method of measuring H<sub>2</sub>S in the vapour phase that is fit for purpose and has the capability of controlling the variables affecting release of H<sub>2</sub>S (sampling method, temperature, V/L ratio and agitation). An ideal method of measuring vapour phase H<sub>2</sub>S should set a single bound condition in terms of temperature and headspace to assess the risk. The temperature and headspace conditions specified should be in the range normally encountered during transport.
- Future work on the flammability of crude oil vapours should be focused on determining the vapour phase composition under specific headspace volumes and temperatures either through equation of state modeling or experimental work, and using those values to determine the upper and lower flammability limits. Consideration should also be given to collection samples of the vapour space in truck tanks and rail cars to enable comparison with field data and laboratory data.
- Compare the dangerous goods classification in the MSDS collected for all samples with the test results to identify any discrepancies.
- Test methods to determine the concentration of H<sub>2</sub>S and hydrocarbons in the vapour phase above produced water under transport conditions would be required to assess the risk that may be present. Consideration should be given to collection samples of the vapour space in truck tanks and rail cars to enable comparison with field data and laboratory data.

## ANNEX B - AITF REPORT (EN)



- 
- Consideration should also be given to collection of a greater number of produced water samples.
  - As a conservative approach, Transport Canada may want to consider requiring a designation such as “Vapour Space may contain Hazardous and/or Flammable Vapours” for produced water that contains H<sub>2</sub>S and/or hydrocarbons above a level set by Transport Canada.

---

## 11 References

- API. (2014). *API RP 3000: Classifying and Loading of Crude Oil into Rail Tank Cars*. Washington DC: American Petroleum Institute.
- Blackmore, T. M. (2014). *Light Ends Composition in Dilbit and Conventional Crudes*. Edmonton: Omnicon Consultants Inc.
- Canadian Trucking Alliance. (2013, November 26). *CTA Issues White Paper on Transportation of Dangerous Goods by Truck*. Retrieved May 27, 2015, from Canadian Trucking Alliance: <http://member.cantruck.ca/imispublic/Home2/AM/ContentManagerNet/ContentDisplay.aspx?Section=Home2&ContentID=13211>
- CAPP. (2014). *Canadian Crude Oil Production by Major Fields*. Calgary: Canadian Association of Petroleum Producers.
- CAPP. (2014). *Crude Oil Forecast, Markets & Transportation*. Calgary: CAPP.
- CAPP. (2014). *Transporting Crude by Rail in Canada*. Calgary: Canadian Association of Petroleum Producers.
- CCQTA. (2014, 05 23). *Analytical Methods*. Retrieved 04 21, 2015, from The Canadian Crude Technical Association: [http://www.ccqta.com/methods.php?analytical\\_id=19](http://www.ccqta.com/methods.php?analytical_id=19)
- Crude Oil Quality Association. (2003). *Water Measurement Subcommittee Final Discussion Paper*. COQA.
- ISO. (2010). *ISO 10156:2010 Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*. Switzerland: International Organization for Standardization.
- Lywood, W. (., & Murray, D. (2012). *H2S in Crude Measurement Report*. Edmonton: Canadian Crude Quality Technical Association.
- Pedersen, K., Thomassen, P., & Fredenslund, A. (1989). Characterization of gas condensate mixtures. *Advances in Thermodynamics*, 137-152.
- Ricciotti, L. (2013, February 18). *Railcars and trucks make a comeback as methods for shipping oil*. Retrieved April 20, 2015, from Alberta Oil Magazine: <http://www.albertaoilmagazine.com/2013/02/railcars-trucks-make-oil-comeback/>

---

White, E., & Montemayor, R. G. (2013). *The Practice of Flash Point Determination: A Laboratory Resource*. West Conshohocken: ASTM International.

CAPP. *Canadian Crude Oil Production by Major Fields*; Table 3.8a; June 2014

J.N. Fox, M.P.B. Nicolas: *Oil in Manitoba: Exploration, production, reserves and revenues*; Manitoba Innovation, Energy and Mines Mineral Resources Division; APEGM Profession Development Seminar; December 5, 2012

M. Yurowski: *Saskatchewan Oil – Hot Plays*; *Saskatchewan Geological Survey*, Saskatchewan Ministry of Energy and Resources; April 18, 2012

Alberta Energy Regulator. ST98-2014; *Alberta's Energy Reserves 2013 and Supply/Demand Outlook 2014-2023*

Alberta Government. *Alberta Oil & Gas Industry Quarterly Update; Winter 2013*

Alberta Government, *Dangerous Goods, Vehicle and Rail Safety Branch*. *A Technical Publication from the Co-ordination and Information Centre: Transportation of Sour Water and Sour Crude Oil*; November 2012

Janicki, E. (2013): *Conventional oil pools of northeastern British Columbia*; BC Ministry of Natural Gas Development, Petroleum Geology Open File 2013-2, 222 pages.

B.C. Oil and Gas Commission. *Energy Briefing Note: The Ultimate Potential for Unconventional Petroleum from the Montney Formation in British Columbia*; November 2013

[www.crudemonitor.ca](http://www.crudemonitor.ca)