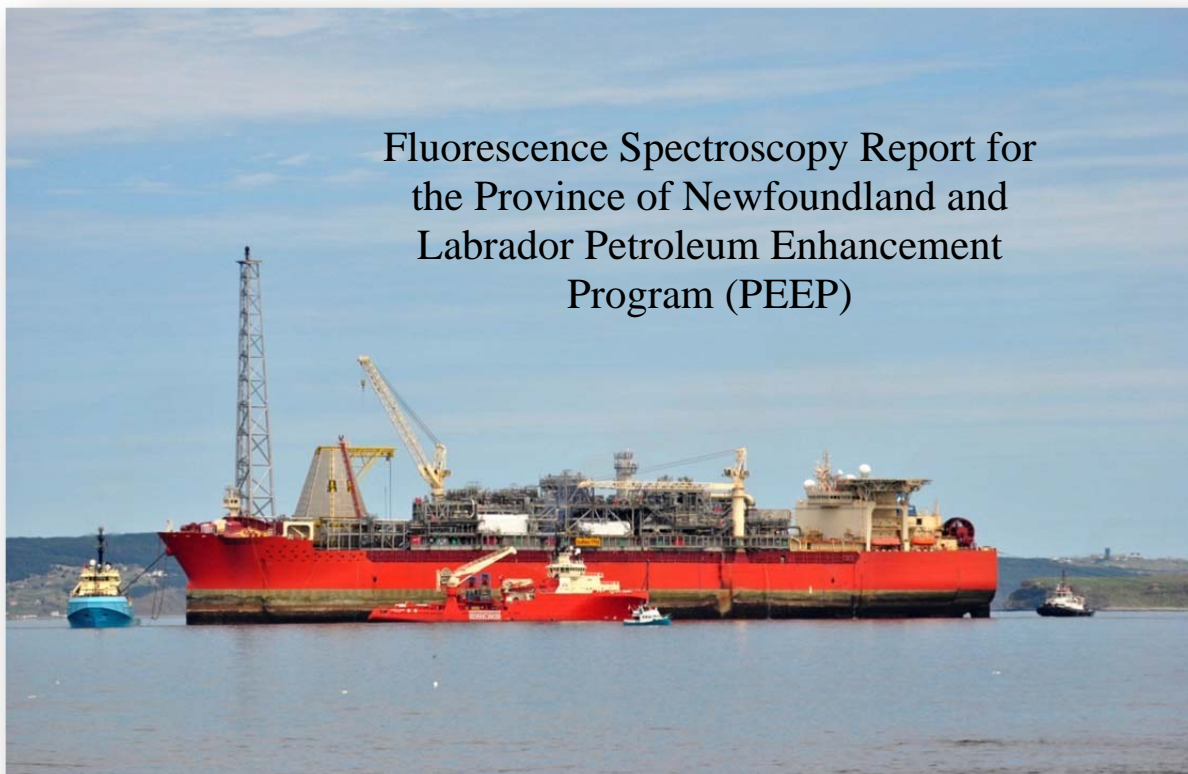




CREAIT Network

## Fluorescence Spectroscopy Report for the Province of Newfoundland and Labrador Petroleum Enhancement Program (PEEP)



Helen Gillespie, Elliott Burden, and Kirk Osadatcz  
2012



# FLUORESCENCE MICROSCOPY REPORT FOR

## Department of Natural Resources

---

### Disclaimer

The Geological Survey of Canada (GSC) organic geochemical data were obtained or compiled by the Department of Natural Resources Canada through the GSC Scientific Laboratory Network Organic Geochemistry and Organic Petrology Laboratory located primarily at GSC Calgary. These data are provided for this project and publication through the Geoscience Data Repository and are copyright of Her Majesty the Queen in Right of Canada, 2007. Although every attempt has been made to ensure that the contents of this data are as accurate as possible, the data are provided on an 'as is' basis. Reprocessing, application of interpretive techniques, and appropriate presentation will enhance the utility of these data. Natural Resources Canada does not assume any liability deemed to have been caused directly or indirectly by any content. For non-commercial and commercial use of the information obtained from the Geoscience Data Repository, please see: Natural Resources Canada [Important Notices <http://www.nrcan.gc.ca/notice\\_e.html>](http://www.nrcan.gc.ca/notice_e.html). For important notices related to use and dissemination of the enclosed data see: [http://www.nrcan.gc.ca/notice\\_e.html](http://www.nrcan.gc.ca/notice_e.html)

These data were produced and/or compiled by Natural Resources Canada for the purpose of providing users with direct access to information about the programs and services offered by Natural Resources Canada. The material in this publication is covered by the provisions of the Copyright Act <<http://laws.justice.gc.ca/en/C-42/index.html>>, other laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission.

Information has been provided for this project with the intent that it be readily available for personal and public non-commercial use and may be reproduced, in part or in whole and by any means, without charge or further permission from Natural Resources Canada. We ask only that:

- Users exercise due diligence in ensuring the accuracy of the materials reproduced;
- Natural Resources Canada be identified as the source department; and,
- The reproduction is not represented as an official version of the materials reproduced, nor as having been made, in affiliation with or with the endorsement of Natural Resources Canada.

Excepting this report, the reproduction of multiple copies of materials this data, in whole or in part, for the purposes of commercial redistribution is prohibited except with written permission from the Government of Canada's copyright administrator, Public Works and Government Services Canada (PWGSC). Through the permission granting process, PWGSC helps ensure individuals/organizations wishing to reproduce Government of Canada materials for commercial purposes have access to the most accurate, up-to-date versions. To obtain permission to reproduce materials on this site for commercial purposes, please go to PWGSC's "Applying for Copyright Clearance on Government of Canada Works" <<http://publications.gc.ca/helpAndInfo/cc-dac/application-e.html>>".

Public Works and Government Services Canada  
Publishing and Depository Services  
350 Albert Street, 4th floor  
Ottawa, Ontario  
Canada  
K1A 0S5

or

email: [copyright.droitdauteur@pwgsc.gc.ca](mailto:copyright.droitdauteur@pwgsc.gc.ca) <<mailto:copyright.droitdauteur@pwgsc.gc.ca>>

Users should be aware that this information is being offered by a non-GoC entity that is not subject to the Official Languages Act <<http://laws.justice.gc.ca/en/O-3.01/index.html>> and to which Natural Resources Canada links, may be available only in the language(s) used by the sites in question.

Natural Resources Canada does not assume any liability deemed to have been caused directly or indirectly by any content provided for this project.

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

## **PART 1:**

### **FLUORESCENCE MICROSCOPY AS A TOOL TO DETERMINE THE THERMAL MATURATION AND API GRAVITY OF NATURALLY OCCURRING CRUDE OILS OR OIL BEARING FLUID INCLUSIONS WITHIN NEWFOUNDLAND AND LABRADOR**

Information on how data can be used as a proxy to determine the thermal maturation and API Gravity of naturally occurring crude oils or oil bearing inclusions within Newfoundland and Labrador.

## **PART 2:**

### **COD a CRUDE OIL DATABASE**

Information on electronic files and their search functions, including an explanation on the Crude Oil Database's construction and how to access its data.

As Proposed by: Helen Gillespie<sup>a</sup>, Elliott Burden<sup>b</sup>, and Kirk Osadetz<sup>c</sup>.

a) Research Laboratory Co-ordinator, CREAT Network, Memorial University of Newfoundland.

b) Professor, Department of Earth Science, Memorial University of Newfoundland.

c) Head of Energy Geoscience Subdivision, Geological Survey of Canada, Calgary.

This report is prepared for the Department of Natural Resources in fulfillment of a PEEP (Petroleum Exploration Enhancement Program) Grant to Helen Gillespie, Elliott Burden, and Kirk Osadetz.

Date: November 30, 2012

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

**PART 1 of 2: Written Report**

**FLUORESCENCE MICROSCOPY AS A TOOL TO  
DETERMINE THE THERMAL MATURATION AND API  
GRAVITY OF NATURALLY OCCURRING CRUDE OILS OR  
OIL BEARING FLUID INCLUSIONS WITHIN  
NEWFOUNDLAND AND LABRADOR**

As Proposed by: Helen Gillespie<sup>a</sup>, Elliott Burden<sup>b</sup>, and Kirk Osadetz<sup>c</sup>.

a) Research Laboratory Co-ordinator, CREAT Network, Memorial University of Newfoundland.

b) Professor, Department of Earth Science, Memorial University of Newfoundland.

c) Head of Energy Geoscience Subdivision, Geological Survey of Canada, Calgary.

A Report Prepared for the Province of Newfoundland and Labrador Petroleum Exploration Enhancement Program (PEEP).

Date: November 30, 2012

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---



**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR  
Department of Natural Resources, Part 1 of 2.**

---

TABLE of CONTENTS	Page
Abstract.....	01
Introduction.....	02
Methodology.....	03
Samples Studied.....	03
Experimental.....	05
Data Interpretation.....	08
Conclusions.....	14
Limitations of the data.....	14
Applications.....	15
Future work.....	15
Acknowledgements.....	16
References.....	16
Appendices.....	18

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

## **FLUORESCENCE MICROSCOPY AS A TOOL TO DETERMINE THE THERMAL MATURATION AND API GRAVITY OF NATURALLY OCCURRING CRUDE OILS OR OIL BEARING FLUID INCLUSIONS WITHIN NEWFOUNDLAND AND LABRADOR**

### **ABSTRACT**

Fluorescence spectrograms for oil samples contain a variety of peaks and shoulders that are generally defined by  $\lambda_{\max}$  (peak of maximum intensity) and a  $Q_{\text{value}}$  (the ratio of the 650 nm intensity /500 nm intensity). Given data from the Crude Oil Database (Part 1 of this report), two sets of quantitative spectral fluorescence experiments on 155 oils and condensates from Newfoundland and Labrador are compared with physical (API gravity) and gross geochemical including Saturates, Aromatics, Resins and Asphaltenes (SARA) properties. These experiments show the sensitivity of the instrument for measuring fluorescence behaviour of petroleum properties.

In the first experiment, fluorescence spectrograms of crude oil samples (excitation fixed wavelength of 365 nm) from the Jeanne d'Arc Basin, show that with increasing thermal maturation and changes in oil geochemistry, there is a continuous shift from a maximum wavelength of 574.57 nm (yellow-green) to 437.30 nm (blue) for light crude (high API gravity). In addition, specific shoulders and secondary peaks that affect the  $Q_{\text{value}}$  correspond with systematic variations in the concentration of total hydrocarbons and an increase in the concentration of saturate fractions.

In the second experiment, the sensitivity of the instrument to subtle variation in oil chemistry is measured against duplicate sets of differentially curated, refrigerated and non-refrigerated oil samples originally collected from exploration programs. Changes in oil quality and UV Fluorescence indicate significant sample degradation in unrefrigerated materials. Replicate measurements indicate that oil samples should be fully analyzed immediately after the crude is first collected and then properly sealed and curated for future use.

By using Fluorescence Spectra curves for oils where API gravity and various geochemical components are known, the quality of unknown oil can now be inferred. Fluorescence Microscopy is an inexpensive and easily produced proxy for oil quality of unknown crude oils or fluid inclusions.

## FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

### INTRODUCTION

As petroleum exploration in Newfoundland and Labrador grows, there is an emerging demand for fluorescence spectroscopy and petroleum fluid inclusion work on this valuable resource. Memorial University is well positioned with respect to fluorescence microspectroscopy and fluid inclusion microscopy. With key equipment in place and a searchable database of existing crude oils analyses available (Part 1 of this report), any new oil analyses from Newfoundland and Labrador can now be easily compiled and displayed. The existing data contains 155 petroleum samples from 52 different wells. Additional new data, in the form of steady state, epi-fluorescence spectrograms for available crude oils have now been added to data we have compiled from a variety of sources including the CNLOPB (Canadian Newfoundland and Labrador Offshore Petroleum Board) and the GSC (Geological Survey of Canada) TABLE 1.

ORGANIZATIONS THAT PROVIDED INFORMATION TO THE DATABASE	TYPE OF DATA PROVIDED
MUN (Memorial University of Newfoundland, CREAT Network)	Oil collection and Fluorescence spectrograms. Date: year 2011.
Husky Energy	Oil samples and well information. Date: year 2011.
CNLOPB (Canadian Newfoundland and Labrador Offshore Petroleum Board)	Oil samples and well information, including API gravity data. Date: at time of drilling.
GSC (Geological Survey of Canada, Calgary Division)	Geochemical Information including: SARA (% saturates, aromatic, resins and asphaltenes), C <sub>5</sub> -C <sub>8</sub> and C <sub>10</sub> -C <sub>32</sub> chromatographs, along with appropriate reports. Date: prior to year 2001 as well as new data collected in 2011.
Petroforma Inc., St. John's, NL	Current API gravity data collected for this project. Date: year 2011.

TABLE1: A list of Organizations that provided data to this project.

The information contained in this report may be used for a variety of purposes in exploration and production and there is ample room for the input of additional data and parameters as they become available. Here, with our addition of Fluorescence Microspectroscopy methods and fluorescence spectrograms to the existing database, we show how relatively simple and rapid microspectroscopy can be used to infer the API gravity and geochemistry of an unknown crude oil or a petroleum fluid inclusion from the Jeanne d'Arc Basin.

The fluorescence behaviour of crude oils as well as its relationship with regard to thermal maturation and degradation has been reviewed by Ryder and Blamey [1] as well as Ryder [2] and the reader is referred to those two references for a broader discussion of the topic and a more thorough review of the literature. In summary, crude oils, typical samples for conventional geochemical investigations, are ideally suited for Fluorescence Microspectroscopy in that under ultraviolet radiation microscopic quantities of oil can exhibit a measureable spectrum of fluorescence which varies in intensity and colour. UV fluorescence spectroscopy cannot only detect the presence of oil but it can also be used to deduce bulk physical and chemical properties.

Fluorescence measurements on crude oils come from the superposition of individual spectra of numerous hydrocarbon and non-hydrocarbon components Dumke and Teschner [3]. Dumke and Teschner agreed with earlier workers [4 to 8] that the fluorescence spectrum of a petroleum sample is systematically shifted to higher wavelengths by increasing the number of aromatic rings and /or introduction of hetero atoms into a molecule. Such systematic alteration of oil and its change in fluorescence is known to occur during naturally occurring processes such as thermal maturation or biodegradation [3, 7 to 13]. For these reasons, fluorescence based methods are increasingly valued for the analysis of crude oils because they offer high speed, low cost, non-contact, and non-destructive testing options for very small micro quantities of oil.

## **METHODOLOGY**

### **SAMPLES STUDIED**

Quantitative spectral fluorescence measurements were made on 155 oils and condensates, from 52 wells of Newfoundland and Labrador. Prior to our collection for this project, oils held by the CNLOPB were in Mason jars and in unrefrigerated storage for a considerable amount of time (up to 20 years in some instances). Many are thought to have lost a significant amount of aromatics. A subset of the CNLOPB's oil samples was collected and analysed by GSC in the early 1990's and subsequently kept refrigerated. As of 2011 oil samples stored at the CNLOPB's storage facility are frozen.

Attempts by the authors to secure fresh samples from specific horizons in producing fields (Hibernia, Terra Nova and White Rose), were generally unsuccessful. Amongst the offshore operators, only Husky Oil was able to provide fresh material from a series of delineation wells. Unfortunately, their samples do not provide much variation in fluorescence. All their samples (Mun0128-Mun0133) come from the same reservoir and show similarity in fluorescence and API gravity. Unable to acquire more recent samples, within the time frame of this report, the authors had no recourse but to work with the samples available from the CNLOPB and the GSC.

As a first indicator for improper storage and degradation it was deemed appropriate to re-run the API gravity on all samples. API gravity, in this instance, acts as a guide to the condition of the samples (changes in API gravity are equated with changes in geochemistry). API gravity is a parameter that is best used to describe crude oil density the higher the API gravity, the lighter, less biodegraded the oil. It should be noted here that all 155 fluorescence spectrograms included in the database show the current API gravity (as they were stored at CNLOPB in September 2011). This current API gravity does not always match the API gravity value in the original drill stem test published by the CNLOPB. In addition, current API gravity values may not reflect the geochemistry provided by the GSC between 1997 and 2001. For analyses collected long after a well is drilled, readers should take care to note when samples were collected and analysed. These records are included in the Database and in this report.

API gravity measurements collected in the fall of 2011 are compared with the original API gravity values recorded during initial exploration (APPENDIX 1). The largest changes occur among the condensates, where, in one instance, the API gravity (Mun0081) has dropped from a high of 62.5° to 43°. Geochemistry indicates that this drop in API gravity is related to changes in the aromatic fraction. Since API gravity values are known to have changed between the times of the original drill stem test until now, we expect the geochemistry of all oils stored with the CNLOPB has changed.

It was not possible (financially or logistically) to repeat the geochemical analyses of all 155 samples to measure the level of degradation. Instead a subset of samples was selected for repeat geochemistry. They represent a variety of different oil types with diverse API gravity, geochemistry and fluorescence spectra.

This subset of samples, collected from the CNLOPB in the fall of 2011, was sent to the GSC in Calgary with instructions to duplicate their (1997-2001) geochemical analyses.

To continue with this measure of degradation of sample quality and fluorescence, the Geological Survey sent a subset of their own CNLOPB oil samples (which were collected at a much earlier date) to Memorial University for fluorescence analyses. Their samples

are assigned MUN numbers (Mun0135-Mun0160). GSC samples are thought to be in better condition than those currently stored at the CNOLPB; they had been refrigerated longer. With better curation one might expect GSC samples to more closely represent the original API gravity and geochemistry. The results (new geochemistry on the MUN samples and new Fluorescence on the GSC samples) are listed in TABLE 2. This list provides comparative information (then and now) on the percentages of the various SARA (saturate, aromatic, resin and asphaltene) fractions, their API gravity values and Fluorescence measurements ( $\lambda_{\max}$  and  $Q_{\text{value}}$ ). It also shows how the data has changed over time.

A triplot of the various geochemical fractions contained in TABLE 2 is illustrated in FIGURE 1. When comparing the chemical composition of the samples collected by Memorial University (this project 2011) to those collected by GSC (1997-2001) there appears to be a decrease in aromatics. This is also reflected in the lower API gravity values for MUN's most recently collected samples from the CNLOPB (TABLE 2). This shift in geochemistry likely reflects the quality of handling and storage employed by GSC vs. that of the CNLOPB. CNLOPB only started to refrigerate their samples in the spring of 2011 after years of improper storage.

### **EXPERIMENTAL**

Using an established UV Fluorescence Spectroscopy Method developed by Tsui [13] (see FIGURE 2) known samples from the Jeanne d'Arc Basin can be used to infer the quality of unknown petroleum resources within this basin. For the context of this report API gravity and the gross geochemistry, provided by gasoline range and saturate fraction gas chromatograms, are referred to as oil quality.

Quality of the crude oil (API gravity, and the Gasoline Range and Saturate Fraction Gas Chromatograms) and Fluorescence Spectrograms are determined through analytical methods outlined in APPENDIX 2 [14-16]. Our readers are referred to this appendix for an in depth description of methods used by different organizations for data collection.

In order to interpret oil quality from the fluorescence spectrum of any unknown oil or from an oil bearing fluid inclusion relationships between these parameters have to be established. In this report a systematic illustration of these different relationships is outlined and discussed.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR

### Department of Natural Resources, Part 1 of 2.

New 2011, Geochemistry data for MUN samples and new Fluorescence data for the same GSC's samples. All other MUN and GSC data remains the same as in the database. Note: Geochemistry data has been normalized, thus the difference with that of the Curde Oil Database information.							
Sample #	Normalized wt.% hydrocarbons	Normalized wt % resins and asphaltenes	Normalized wt% saturates	Normalized wt% aromatics	API°gravity	$\lambda_{max}$	Q <sub>value</sub>
Mun0004 (CNLOPB)	99.05	1.0	90.4	8.7	46.2	438	0.08
L00097 (GSC)	99.45	0.6	85.6	13.8	54.0	439	0.08
Mun0005	99.49	0.5	91.6	7.9	46.6	438	0.08
L00143	97.62	2.4	87.8	9.9	58.6	439	0.06
Mun0037	75.83	24.2	41.8	34.0	17.9	495	0.49
L00249	81.40	18.6	36.3	45.1	18.3	527	0.35
Mun0038	78.80	21.2	44.9	33.9	19.2	530	0.49
L00248	86.80	13.2	42.3	44.5	19.0	527	0.35
Mun0094	82.94	17.1	56.0	26.9	20.7	526	0.31
L00455	89.20	10.8	48.0	41.2	21.6	527	0.28
Mun0013	81.60	18.4	49.8	31.8	24.3	527	0.35
L00166	85.74	14.3	39.7	46.0	24.0	527	0.35
Mun0012	82.16	17.8	48.2	33.9	24.8	528	0.38
L00167	86.74	13.3	39.5	47.3	25.6	527	0.33
Mun0022	83.90	16.1	55.5	28.4	25.4	528	0.35
L00183	91.82	8.2	53.2	38.6	26.0	527	0.29
Mun0014	84.71	15.3	53.7	31.0	28.8	528	0.34
L00171	91.32	8.7	47.7	43.6	29.1	526	0.25
Mun0025	97.29	2.7	83.6	13.7	45.0	438	0.04
L00220	98.07	1.9	73.5	24.6	47.2	439	0.04
Mun0027	96.70	3.3	85.1	11.6	48.7	438	0.04
L00218	97.93	2.1	71.3	26.6	52.8	439	0.04
Mun0029	98.50	1.5	86.1	12.3	48.1	438	0.04
L00217	98.26	1.7	75.0	23.2	53.2	439	0.04
Mun0030	95.61	4.4	71.6	24.0	37.2	492	0.07
L00222	94.30	5.7	59.3	35.1	37.3	492	0.10
Mun0075	82.15	17.8	49.7	32.5	26.4	527	0.36
L00382	84.73	15.3	46.1	38.6	31.7	492	0.28
Mun0009	90.62	9.4	64.3	26.3	31.3	495	0.25
L00151	91.83	8.2	51.8	40.0	32.3	492	0.17
Mun0087	91.95	8.1	63.8	28.1	34.2	494	0.16
L00433	94.94	5.1	60.8	34.2	34.7	495	0.15
Mun0098	91.73	8.3	68.1	23.6	29.4	495	0.18
L00484	91.56	8.4	57.1	34.5	34.1	492	0.36
Mun0102	91.59	8.4	67.5	24.1	28.0	495	0.22
L00480	91.93	8.1	53.7	38.3	32.0	495	0.17
Mun0107	90.61	9.4	62.8	27.8	28.0	495	0.24
L00789	90.65	9.3	52.6	38.1	34.8	492	0.18
Mun0024	94.19	5.8	69.7	24.5	36.0	494	0.09
L00190	94.31	5.7	62.1	32.3	36.1	494	0.11
Mun0134	53.89	46.1	21.2	32.7	11.0	573	0.79
n/a							

TABLE 2: Sub-set of samples from the Newfoundland and Labrador crude oil database. MUN numbers represent those samples acquired recently from CNOLPB by Memorial University. The GSC samples, acquired between 1997 and 2001, have numbers with the prefix L#. All sample information is available in the Crude oil Database.



## FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

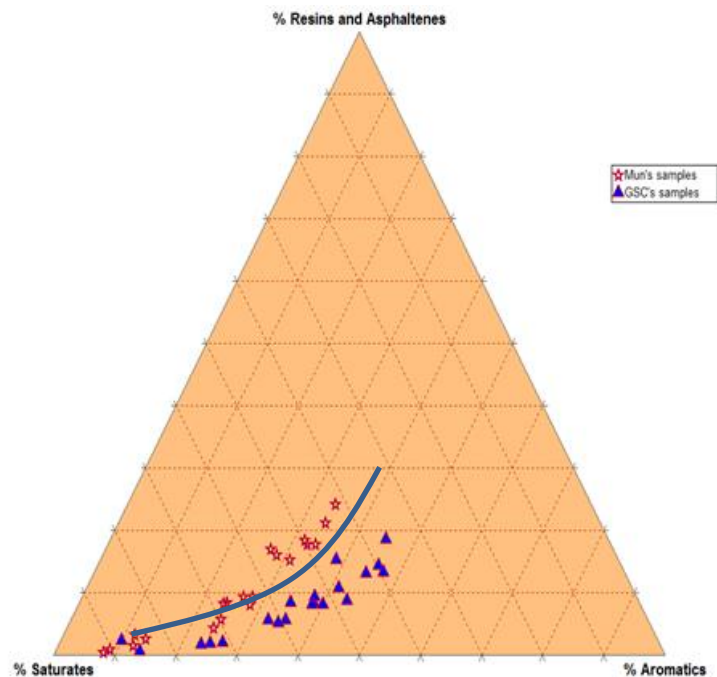


FIGURE 1: Ternary diagram of the gross chemical composition of MUN samples (red star) as currently stored at CNLOPB vs. the same CNLOPB samples collected and analysed by the GSC (blue triangle) prior to 2001. MUN samples show a lower concentration of the aromatic fraction.

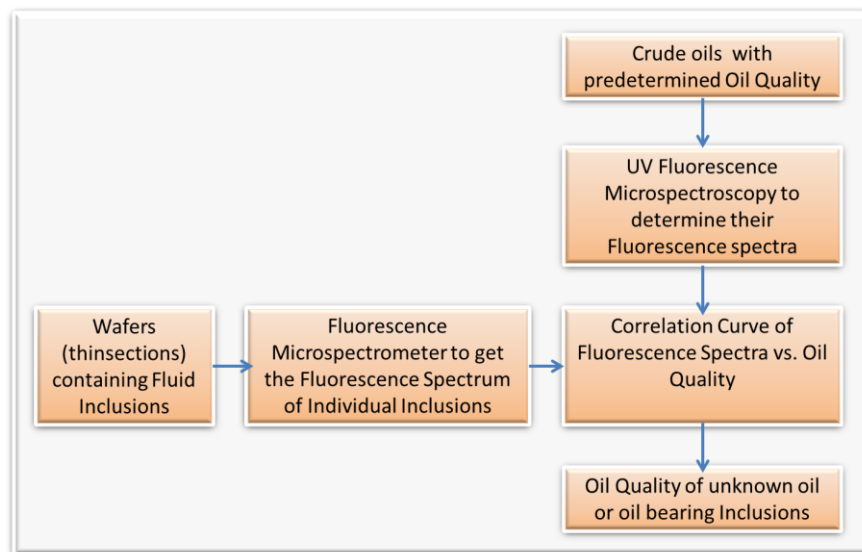


FIGURE 2: Flow diagram, illustrating a method to characterize oil quality from an unknown oil or an unknown oil bearing fluid inclusions, via UV Fluorescence Microspectroscopy. After Tsui [13].

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

When visually comparing or characterizing fluorescence emission spectra of crude oils for qualitative analyses, similarities and differences in their shape are observed. Two features in particular are taken into consideration:  $\lambda_{\max}$  (wavelength of maximum peak intensity) and the position of any secondary peaks that may occur as shoulders. Samples are visually compared and grouped by noting the changes in the position and intensity of these peaks.

With quantitative analyses three values in particular are considered, API gravity,  $\lambda_{\max}$  and Q value. API gravity describes crude oils density.  $\lambda_{\max}$  refers to wavelength of maximum intensity and the  $Q_{\text{value}}$  which is a colourimetric quotient defined as a ratio of the intensity at 650 nm to the intensity at 500 nm ( $Q_{\text{value}} = \text{Intensity}_{650\text{nm}} / \text{Intensity}_{500\text{nm}}$ ). Both spectra values ( $\lambda_{\max}$  and  $Q_{\text{value}}$ ) are read from the fluorescence spectrogram (FIGURE 3). The API gravity value is determined from other lab analyses for oils [15].  $\lambda_{\max}$  and the  $Q_{\text{value}}$  are known to correlate positively with oil density, API gravity and geochemistry [8, 9, 11-14, 17-19].

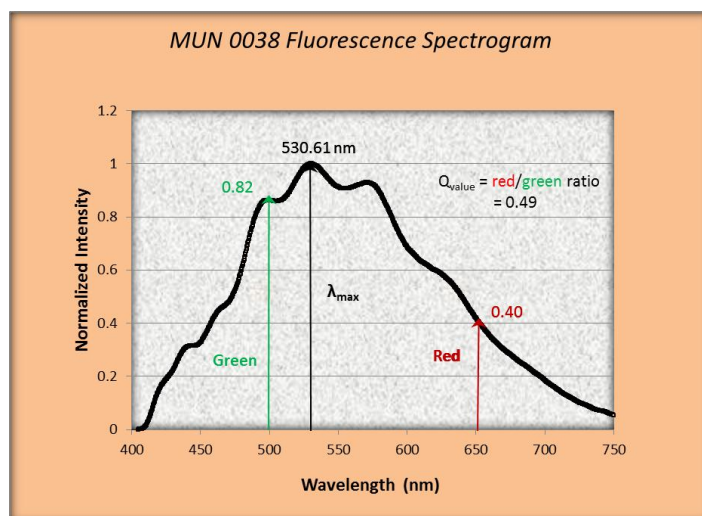


FIGURE 3: Fluorescence spectrum showing measurement of  $\lambda_{\max}$  and Q value.  $\lambda_{\max}$  is the wavelength of maximum intensity and  $Q_{\text{value}}$  is the red/green quotient.

### DATA INTERPRETATION of the FLUORESCENCE GRAPHS

The  $\lambda_{\max}$  values for all 155 crude oil samples analysed (APPENDIX 3) range from 437.30 nm (Mun0080) to 574.57 nm (Mun0001), whereas the values for Q range from 0.06 (Mun0005) to 0.79 (Mun0134). As a demonstration in the use of this database we have chosen six fluorescence spectra (FIGURE 4) from crude oils from the Jeanne d'Arc Basin to show how the overall shape of fluorescence spectra and the position of  $\lambda_{\max}$  vary according to changes in API gravity and gross geochemistry.

# FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

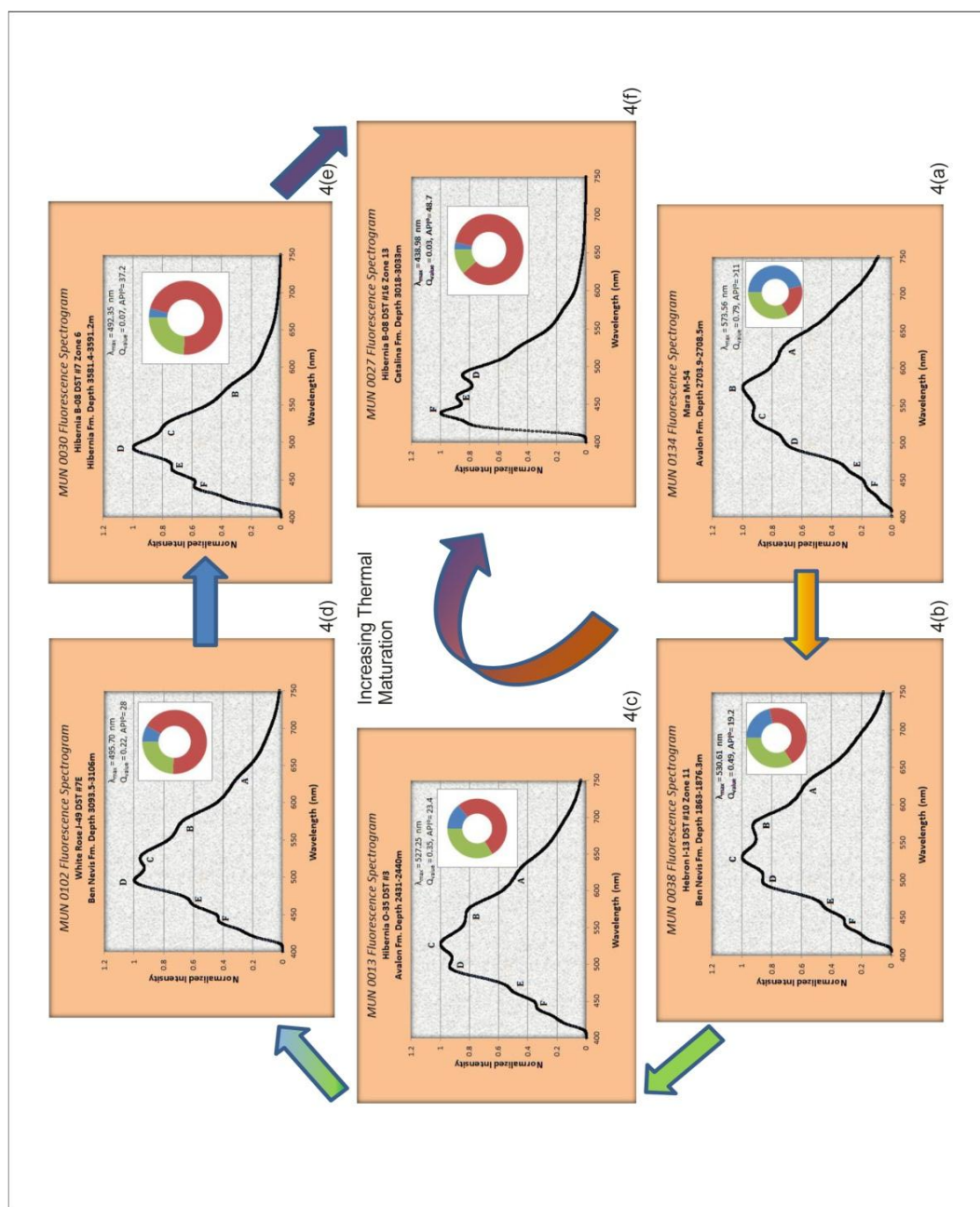


FIGURE 4: An Illustration of how fluorescence is influenced by changes in oil quality. Donut shape insert refers to percent saturates (red), aromatics (green), and resins and asphaltenes (blue).

Six highlighted areas of interest, labelled A to F, are identified from the spectrograms (FIGURE 4). As oils become thermally mature, or during migration, through the selective removal of the heavier heteroaromatic and aromatic compounds [13], a gradual decrease in the aromatic-to-saturate ratio develops. These six peak areas reflect this change in oil quality with a progressive shift in fluorescence to lower wavelengths. Lamda max can be seen to shift from B (573.56 nm) in FIGURE 4a through to f (438.98 nm) in FIGURE 4f. This shift is also evident with changes in the  $Q_{\text{value}}$  which decreases from 0.79 to 0.04. API gravity and the various SARA fractions (the small donut insert associated with the spectrograms) show systematic trends consistent with fluorescence change. The API gravity values increase from  $11^{\circ}$  to  $48.7^{\circ}$  indicating a change in the density of the oils. So too, the concentration of the total hydrocarbons and saturate fractions increases from 53.89% to 96.70% and 21.2% to 85.1% respectively (values used in FIGURE 4 are as seen in TABLE 2).

Once relationships between Fluorescence, API gravity and Geochemistry are established, (TABLE 2 and FIGURE 4), then by comparison of an unknown oil fluorescence spectrum to that of the existing known spectra, the quality of the unknown can be described.

To test the use of fluorescence spectra to accurately predict oil quality (in this case API gravity) we have plotted, in FIGURE 5a and 5b, two data sets containing fluorescence and API gravity data on all oil samples listed in the Crude Oil Database (APPENDIX 4). One set (FIGURE 5a) shows a correlation for oil samples where Fluorescence and API gravity were collected during the same year (2011). In contrast, FIGURE 5b shows a correlation for the same oil samples wherein Fluorescence was collected in 2011 but the API gravity was collected years earlier (perhaps during drill stem testing, and certainly prior to 2001). The higher correlation coefficient of  $R^2=0.8097$  in FIGURE 5a versus  $R^2=0.6839$  of FIGURE 5b is attributed to the quality of the samples. We believe that fluorescence spectra will provide the best correlation with oils API gravity when both analyses are taken within the same time frame and before a sample has become degraded (e.g. FIGURE 5b).

In another test, using fluorescence spectra to accurately reflect oil quality (in this case geochemistry as well as API gravity), we compiled data on a subset of samples from the crude oil database. One dataset was collected from the CNLOPB by MUN and another duplicate set was collected from the CNLOPB and other unspecified locations by the GSC (TABLE 2). Both sets of data from the same oil samples were collected at different times. MUN's samples were collected from the CNLOPB in 2011 and all analyses (fluorescence, geochemistry and API gravity) were carried out in that year.

**FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

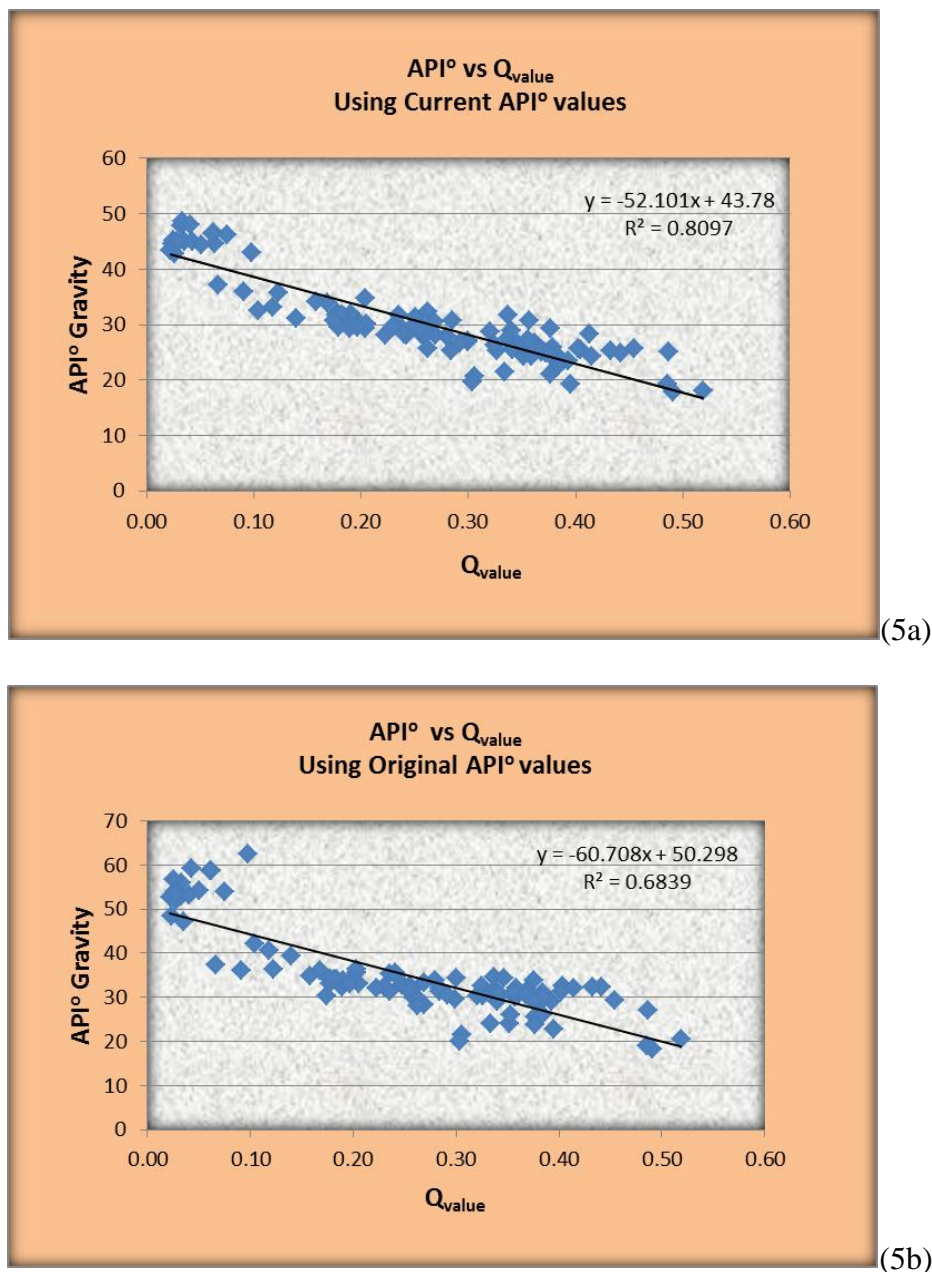


FIGURE 5: Relationships between Fluorescence (Q<sub>value</sub>) and API gravity. Chart (5a) depicts samples relationship using recently collected fluorescence measurement (Q<sub>value</sub>) and recently collected API gravity measurements whereas chart (5b) illustrates the same relationship using recently collected Q values and older (API gravity values).

GSC samples were collected and analysed at various times after wells were completed and before 2001. Inasmuch as their samples were refrigerated, fluorescence on refrigerated samples (measured in 2011) presumably reflects the geochemistry and API



gravity at the time they were cooled. In other words, once refrigerated the samples have not changed significantly or degraded.

As such, we thought it appropriate to plot this data to determine if changes have occurred between the time when the GSC made their measurements and more recently when MUN had collected their data. Plots of  $Q_{\text{value}}$ , (read from the collected fluorescence spectrograms), API gravity and various SARA fractions (Saturates, Aromatics, Resins and Asphaltenes) for the two data sets (TABLE 2) are illustrated in FIGURE 6a, b and c.

In this figure, MUN samples collected from the CNOLPB (2011) show the best relationships with the higher correlation co-efficient of  $R^2=0.8472$ ,  $0.8780$  and  $0.9482$  for API gravity vs.  $Q_{\text{value}}$ , Saturates vs.  $Q_{\text{value}}$  and % Hydrocarbons vs.  $Q_{\text{value}}$  respectively. In contrast, comparing current fluorescence measurements for GSC samples with chemistry analysed years ago, consistently show lower values for API gravity vs.  $Q_{\text{value}}$  ( $R^2=0.7625$ ), Saturates vs.  $Q_{\text{value}}$  ( $R^2=0.7261$ ) and % Hydrocarbons vs.  $Q_{\text{value}}$  ( $R^2=0.7815$ ).

We believe the higher correlation co-efficients for MUN samples are simply a function of the collection dates. For MUN data, the fluorescence, API gravity and geochemistry are all new collected within a six month time frame. On the other hand, GSC samples were collected and analysed at significantly different dates. It appears that even with refrigeration GSC samples have undergone a certain amount of change; fluorescence for these samples does not show correlation values one might expect if the samples were completely stabilised. It may be that with even the best storage options available it will remain extremely difficult to keep a crude oil fresh.

The data in TABLE 2 accurately represent the quality of the oil currently stored with the CNLOPB in St. John's and the GSC facility in Calgary. Unfortunately none of these samples, except perhaps the most recent samples from White Rose (Mun0128-013), represent the actual quality of crude oil in the reservoir.

The lesson from this brief comparison is clear. In order to accurately determine crude oil properties (API gravity and bulk geochemistry, and microfluorescence), all analyses should be done immediately upon collection, and well before an oil sample has had time to deteriorate. Only then, will correlation diagrams provide the best available data to infer oils quality with regard to its API gravity and geochemistry. In addition, to reduce degradation, reference samples must be well sealed and kept in cold storage.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

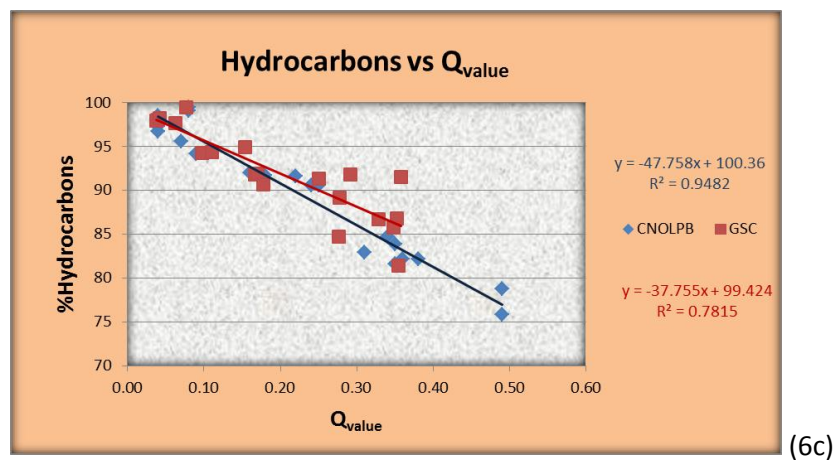
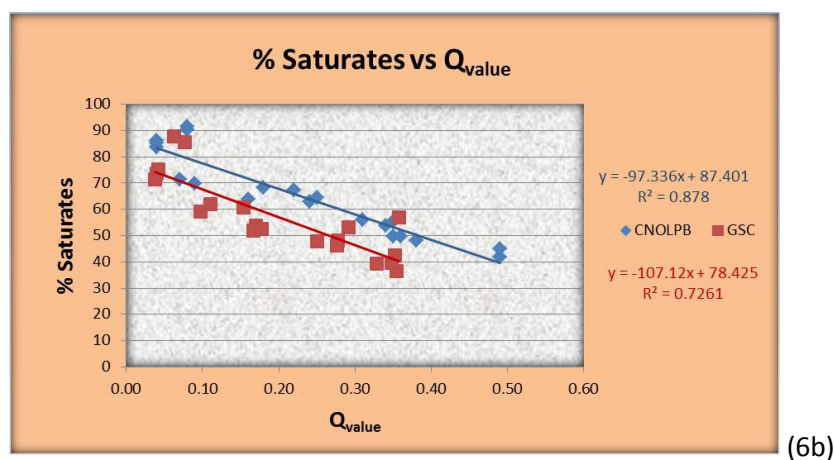
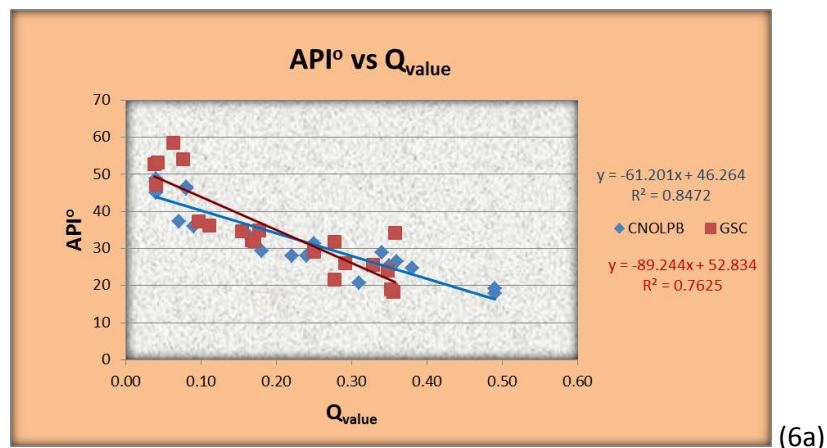


FIGURE 6a, b, and c: Relationships between Fluorescence and Oil Quality for those oil samples stored at the CNOLPB (those collected and analysed by MUN in 2011) and those collected and stored in Calgary by the GSC (between 1997-2001). Data from TABLE 2 of this report.

## CONCLUSIONS

In total, data on 155 crude oil samples are compiled into the enclosed Crude Oil Database (PART 2 of this report). This database provides new Quantitative Spectral Fluorescence measurements that can be used in conjunction with recent API gravity and geochemistry to infer the oil quality of an unknown oil sample within Newfoundland and Labrador. This can be done through comparison of the unknown oils fluorescence spectrum to that of known fluorescence spectrums like those represented in the Maturation Diagram of FIGURE 4.

We have confirmed earlier reports/publications that Fluorescence measurements ( $\lambda_{\max}$  and  $Q_{\text{value}}$ ) correlate positively with oil density (API gravity) and geochemistry in that lighter oils show emissions at lower wavelengths than heavier oils. Also we have shown that Fluorescence spectra of oils from within the Jeanne d'Arc Basin show a progressive decrease in the  $\lambda_{\max}$  (blue shift) and  $Q_{\text{value}}$  with: i) increasing API gravity, ii) increasing concentration of total hydrocarbons; and iii) increasing concentration of saturate fraction. For these reasons we believe that the data in this report along with the information provided in the attached database can be used to infer oil quality of an unknown oil sample or its fluid inclusion from within the Jeanne d'Arc Basin.

### LIMITATIONS in the use of database

We recommend (due to the condition of the oil samples) that the use of the fluorescence data to infer the quality of an unknown oil sample be limited to those samples listed in TABLE 1 of the written part of this report or from the database samples where API gravity and geochemistry have not changed significantly (perhaps within 1 or 2 degrees API) from the time when they were collected. Where possible we recommend that the user measure oil quality as soon as the sample is collected through proper analytical methods.

The use of fluorescence based methods to infer oil quality should be limited to samples where proper analytical methods are available for preliminary investigations in a study region.

The fluorescence charts in the Crude Oil Database can only be used to infer present API gravity and geochemistry and should not be used to infer the original API gravity and geochemistry when the wells were completed. Please check the collection dates.



## **FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.**

---

The various data sets included in the Crude Oil Database can and should be used independent of the fluorescence data. End users are reminded to notice collection dates should they choose to use data for other scientific purposes.

Due to the highly complex nature of fluorescence and fluid composition, users are reminded that empirical relationships shown between fluorescence properties, oil geochemistry and API gravity, will probably work best for genetically related petroleum fluids and should only be used as a qualitative guide when used to determine oil quality in another basin.

### **APPLICATIONS in the use of database**

This information may be useful in basin analysis studies to:

1. estimate the maturation of reservoir oils;
2. determine direction and distance of crude oil migration;
3. identify source rocks;
4. assist in the solution of migration problems that have been complicated by geological structure; and
5. to determine the migration state of natural petroleum in oil-field waters.

By comparing the fluorescence properties of fluid inclusion oils and reservoir oils, the history of migration in petroleum basins can be reconstructed.

### **FUTURE WORK**

The information provided in the Crude Oil Database provides an excellent source of information to further oil related studies. We recommend that information on new oil shows (or discoveries) be added to the database as soon as possible, and certainly before the oil has a chance to deteriorate. Appropriate information should include: Sample Information and Well Location Information, Fluorescence, API Gravity and its Geochemistry.

The Maturation diagram, illustrating how fluorescence spectra are influenced with changes in the quality of oil, should be tested on another basin where oil quality has been recently measured or can be characterized along with its fluorescence. We recommend testing the diagram on a recently collected suite of oil samples from a known basin (such as in Western Canada) where recent API gravity and Geochemistry measurements are available. This way we can determine if the changes we see in fluorescence are a function of the petroleum system characteristics or if these changes are in fact universally applicable.

## **ACKNOWLEDGEMENTS**

The authors would like to thank the Department of Natural Resources and Nalcor Energy for their financial support and Mark Obermajer at the Geological Survey for his analytical expertise,

In addition the lead author would like to thank Dr. Nigel Blamey for his encouragement and for the many conversations discussed over numerous cups of tea during his all but too brief visits to Newfoundland.

## **REFERENCES**

- 1) Ryder, Alan G. and Blamey Nigel J. F. (2009) Hydrocarbon Fluid Inclusion Fluorescence. A Review. *Reviews in Fluorescence*. **2007**:299-334.
- 2) Ryder, Alan G. (2005) Analysis of Crude Petroleum Oils using Fluorescence Spectroscopy. *Reviews in Fluorescence*. **2005**:169-198.
- 3) Dumke, I. and Teschner, M. (1988) Application of fluorescence spectroscopy to geochemical correlation problems. *Adv. in Org. Geochem.* **13** (4-6):1067-1072.
- 4) Hercules, D.M. (ed.) (1966) Fluorescence and Phosphorescence Analysis. Interscience, New York.
- 5) Beriman I.B. (1971) Handbook of Fluorescence Spectra of Aromatic Molecules, 2<sup>nd</sup> Edition. Academic Press, New York.
- 6) Bertrand, P., Pittion, J., and Bernaud, C. (1986) Fluorescence of sedimentary organic matter in relation to its chemical composition. *Org. Geochem.* **10**:641-647.
- 7) Gijzel, P. van. (1981) Applications of the geomicrophotometry of kerogen, solid hydrocarbons and crude oils to petroleum exploration. In: *Organic Maturation Studies and Fossil Fuel Exploration* (Ed. Brooks, J.) pp. 351-377. Academic Press, London.
- 8) Riecker, R. E. (1962) Hydrocarbon fluorescence and migration of petroleum. *AAPG Bulletin*. **46**:60-75.
- 9) Stasiuk, L.D. and Snowdon, R.L. (1997) Fluorescence micro-spectrometry of synthetic and natural hydrocarbon fluid inclusions: crude oil chemistry, density and application to petroleum migration. *Appl. Geochem.* **12**:229-241.
- 10) Lo, H.B. (1987) A Quantitative fluorescence technique for evaluating thermal maturity: Instrumentation and examples. *Org. Geochem.* **11**(5):572-377.

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

- 11) Hagemann, H. and Hollerbach, A. (1985) The fluorescence behavior of crude oils with respect to their thermal maturation and degradation. *Org. Geochem.* **10**:473-480.
- 12) Chang, Y.J. and Huang, W.L. (2008) Simulation of the fluorescence evolution of “live” oils from kerogens in a diamond anvil cell: application to inclusion oils in terms of maturity and source. *Geochim, Cosmochim. Acta.* **72**(15): 3771-3787.
- 13) Tsui (1990) Method for characterizing oil-bearing inclusions via fluorescence microspectrophotometry. *AAPG*.**74**: 781.
- 14) Gillespie, H. and Burden, E.T. (2010) Fluorescence microspectroscopy as a proxy to determine the thermal maturation and API gravity of naturally occurring crude oils. *Internal Report*, CREAT Network, Memorial University. pp. 9
- 15) Petroforma Inc. as per communication, 2011. See Appendix 2 of this report.
- 16) Fowler, M.G. and Obermajer, M.( 2001) Gasoline range and saturate fraction gas chromatograms of Jeanne d'Arc Basin Crude Oils. *Geological Survey of Canada*, Open File **D3945**
- 17) Khorasani, G. K., (1987) Novel development in fluorescence microscopy of complex organic mixtures: Application in petroleum geochemistry. *Org. Geochem.* **11**:157-168.
- 18) Stasiuk L. D., Gentzis T. and Rahimi P. (2000) Application of spectral fluorescence microscopy for the characterization of Athabasca bitumen vacuum bottoms. *Fuel.* **79**:769-775.
- 19) Alpern, M.J., Lemos De Sousa, M.L., Pinheiro, H.J., and Zhu, X. (1993) Detection and evaluation of hydrocarbons in source rocks by fluorescence microscopy. *Org. Geochem.* **20** (6):789-795.

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

**APPENDICES**

**APPENDIX 1**

**LIST OF SAMPLES, AS PROVIDED IN THE CRUDE OIL DATABASE, TABULATING THEIR CURRENT (YR. 2011) AND PREVIOUSLY COLLECTED API GRAVITY.**

API gravity Information				
MUN Sample Number	Extract type	Sampling Date of Original API	Original API of Oils from drill stem test	Current API at 15 degrees (yr.2011)
Mun0001	oil	06-Aug-72	6.7	nul
Mun0002	oil	27-Jul-73	31	28.2
Mun0003	condensate	14-Jul-74	50	44.6
Mun0004	condensate	28-Jul-75	54	46.2
Mun0005	condensate	09-Aug-78	58.6	46.6
Mun0006	oil	27-May-79	31.4	30
Mun0007	oil	27-May-79	32.6	29.5
Mun0008	oil	27-May-79	32.8	29.4
Mun0009	oil	27-May-79	32.3	31.3
Mun0010	oil	27-May-79	30.1	25.7
Mun0011	condensate	30-Jul-79	55.9	47.8
Mun0012	oil	01-Jan-80	25.6	24.8
Mun0013	oil	01-Jan-80	24	24.3
Mun0014	oil	01-Jan-80	29.1	28.8
Mun0015	oil	01-Jan-80	30.3	28.7
Mun0016	oil	01-Jan-80	31.5	27.4
Mun0017	oil	01-Jan-80	30.8	26.6
Mun0018	oil	01-Jan-80	29.2	25.8
Mun0019	oil	10-Jan-80	nul	38.4
Mun0020	oil	10-Jan-80	nul	32.6
Mun0021	oil	10-Jan-80	27	25.1
Mun0022	oil	10-Jan-80	26	25.4
Mun0023	oil	19-Mar-80	33.6	30.8
Mun0024	oil	19-Mar-80	36.1	36.0
Mun0025	condensate	19-Mar-80	47.2	45.0
Mun0026	condensate	19-Mar-80	48.5	44.6
Mun0027	condensate	19-Mar-80	52.8	48.7
Mun0028	oil	19-Mar-80	34.6	31.8
Mun0029	condensate	19-Mar-80	53.2	48.1
Mun0030	oil	19-Mar-80	37.3	37.2
Mun0031	oil	19-Mar-80	nul	46.3
Mun0032	oil	19-Mar-80	42	32.5
Mun0033	oil	19-Mar-80	40.7	33.1
Mun0034	oil	16-Sep-80	39.4	31.2

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

API gravity Information				
MUN Sample Number	Extract type	Sampling Date of Original API	Original API of Oils from drill stem test	Current API at 15 degrees (yr.2011)
Mun0036	oil	14-Jan-81	31	23.8
Mun0037	oil	14-Jan-81	18.3	17.9
Mun0038	oil	14-Jan-81	19	19.2
Mun0039	oil	14-Jan-81	29	23.4
Mun0040	oil	26-Feb-81	32.5	25.5
Mun0041	oil	26-Feb-81	34.4	26.4
Mun0042	oil	26-Feb-81	34.2	26.9
Mun0043	oil	26-Feb-81	29.5	27.1
Mun0044	oil	26-Feb-81	32	24.3
Mun0045	oil	26-Feb-81	30	22.3
Mun0046	oil	26-Feb-81	28.7	23.3
Mun0047	oil	26-Feb-81	32.2	24.8
Mun0048	oil	26-Feb-81	32	24.2
Mun0049	oil	14-Jan-81	36	34
Mun0051	oil	29-Sep-81	31.3	25.6
Mun0052	oil	29-Sep-81	31	25.4
Mun0054	oil	29-Nov-81	32.4	29.8
Mun0055	oil	29-Nov-81	30.3	25.2
Mun0056	oil	29-Nov-81	31.4	30.7
Mun0057	oil	29-Nov-81	32.3	28.3
Mun0058	condensate	13-Dec-82	52.7	43.3
Mun0059	oil	18-Dec-82	30	30.7
Mun0060	oil	18-Dec-82	28.3	30.5
Mun0061	oil	18-Dec-82	nul	26.3
Mun0062	oil	02-Aug-83	32.4	29.3
Mun0063	oil	02-Aug-83	33.4	28
Mun0064	oil	02-Aug-83	15.9	27.9
Mun0065	oil	02-Aug-83	15.9	27.8
Mun0066	oil	08-Aug-83	29.7	27.9
Mun0067	oil	08-Aug-83	35.6	34.7
Mun0068	oil	08-Aug-83	36.3	35.7
Mun0069	oil	08-Aug-83	35.3	31.8
Mun0070	oil	08-Aug-83	29.2	25.6
Mun0071	oil	08-Aug-83	26	23.4
Mun0072	oil	08-Aug-83	31.4	25
Mun0073	oil	09-Aug-83	31.7	29.4
Mun0074	oil	09-Aug-83	29.7	32.4
Mun0075	oil	09-Aug-83	31.7	26.4
Mun0076	oil	09-Aug-83	30.1	24.5
Mun0077	oil	09-Aug-83	31.1	27.2

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

API gravity Information				
MUN Sample Number	Extract type	Sampling Date of Original API	Original API of Oils from drill stem test	Current API at 15 degrees (yr.2011)
Mun0078	oil	09-Aug-83	31	24.9
Mun0079	oil	09-Aug-83	32.2	25.3
Mun0080	condensate	12-Nov-83	59.3	45.0
Mun0081	condensate	12-Nov-83	62.5	43.0
Mun0082	oil	21-Jan-84	30.5	25.4
Mun0083	oil	21-Jan-84	nul	27.1
Mun0085	oil	21-Jan-84	32.6	26.2
Mun0086	oil	21-Jan-84	33.7	27.9
Mun0087	oil	21-Mar-84	34.7	34.2
Mun0088	condensate	21-Mar-84	58.7	46.4
Mun0089	oil	27-Jun-84	32	25.3
Mun0090	condensate	27-Jun-84	56.6	45.2
Mun0091	oil	15-Jul-84	22.8	19.3
Mun0092	oil	15-Jul-84	28.1	25.7
Mun0093	oil	21-Oct-84	20.5	18.1
Mun0094	oil	21-Oct-84	21.6	20.7
Mun0095	oil	05-Nov-84	23.8	21.1
Mun0096	oil	05-Nov-84	29	24.6
Mun0097	oil	18-Dec-84	33.9	29.3
Mun0098	oil	18-Dec-84	34.1	29.4
Mun0099	condensate	18-Dec-84	51.8	44.5
Mun0100	condensate	27-Jul-85	54	42.7
Mun0101	oil	27-Jul-85	30.5	26.7
Mun0102	oil	27-Jul-85	32	28.0
Mun0103	condensate	27-Jul-85	54.1	44.4
Mun0104	oil	05-Sep-85	nul	24.1
Mun0105	oil	26-Nov-85	33	32.2
Mun0106	condensate	18-Dec-85	53.4	44.9
Mun0107	oil	05-Feb-86	34.8	28.0
Mun0108	oil	05-Feb-86	36.2	29.2
Mun0109	oil	05-Feb-86	35.5	28.3
Mun0110	oil	13-Jun-87	34	31.5
Mun0111	oil	13-Dec-87	33.1	30.1
Mun0112	oil	13-Dec-87	34	31.8
Mun0113	oil	05-Mar-88	33.6	31.2
Mun0114	oil	05-Mar-88	33.8	31.9
Mun0115	oil	05-Mar-88	34	31.8
Mun0116	oil	27-Feb-99	nul	22.5
Mun0117	oil	24-Jun-91	33	29.5
Mun0118	oil	31-Jul-97	30.2	30.8

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

API gravity Information				
MUN Sample Number	Extract type	Sampling Date of Original API	Original API of Oils from drill stem test	Current API at 15 degrees (yr.2011)
Mun0119	oil	08-Apr-99	31.5	29.0
Mun0120	oil	30-Dec-98	20.1	19.6
Mun0121	oil	07-Apr-99	nul	27.4
Mun0122	oil	16-Jun-99	nul	28.3
Mun0123	oil	05-Dec-02	nul	20.2
Mun0124	oil	12-Feb-00	24	21.4
Mun0126	oil	08-Feb-03	nul	nul
Mun0127	oil	06-Mar-90	15	nul
Mun0128	oil	27-Jul-11	nul	29.3
Mun0129	oil	03-Sep-11	nul	29
Mun0130	oil	06-Sep-11	nul	29.7
Mun0131	oil	27-Jul-11	nul	29
Mun0132	oil	04-Sep-11	nul	29.4
Mun0133	oil	26-Jul-11	nul	29.1
Mun0134	oil	21-Oct-84	11	nul

## **APPENDIX 2**

### **METHODOLOGY FOR FLUORESCENCE SPECTROSCOPY, API GRAVITY AND GASOLINE RANGE AND SATURATE FRACTION GAS CHROMATOGRAMS**

#### **FLUORESCENCE SPECTROSCOPY METHOD**

This method has been written before in an internal report for CREAT Network [14]. Since it has not been published externally to CREAT it was deemed appropriate to include it here, with minor modification.

#### **EQUIPMENT**

The fluorescence emissions of each crude oil were analyzed using a Craic QD1 202<sup>TM</sup> Microspectrophotometer with an X-Cite series 120 ultraviolet light source. System software, supplied with the unit, was used to collect the fluorescence relative energy versus wavelength data. All data were normalized and graphs were printed in Microsoft Excel.

Linear response of the instrument proved to be accurate when checked at 200, 400, 800, 1600 and 3200 milliseconds on blue, red and green fluorescent standards.

The following equipment was used during fluoranalyses.

- Spectrometer: QD1 202<sup>TM</sup> with a 1Megapixel resolution camera attachment. Spectral range was set to 400-750 nm; spectral bandwidth 0.32 nm, spectral resolution 15 nm, scan time 200 milliseconds and a scan average of 50.
- Microscope: Zeiss Axio Imager; magnification 40x; sampling area 2.5 microns.
- Ultraviolet light source: X-Cite series 120 with a high pressure 120 watt metal halide short arc lamp.
- Visible light source: 12v, 100w halogen bulb.
- Filters: Zeiss filter set 02, catalogue # 488002-9901-000. Excitation G 365, beam splitter FT 395, emission LP 420. (Figure 1, see below).



## FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.

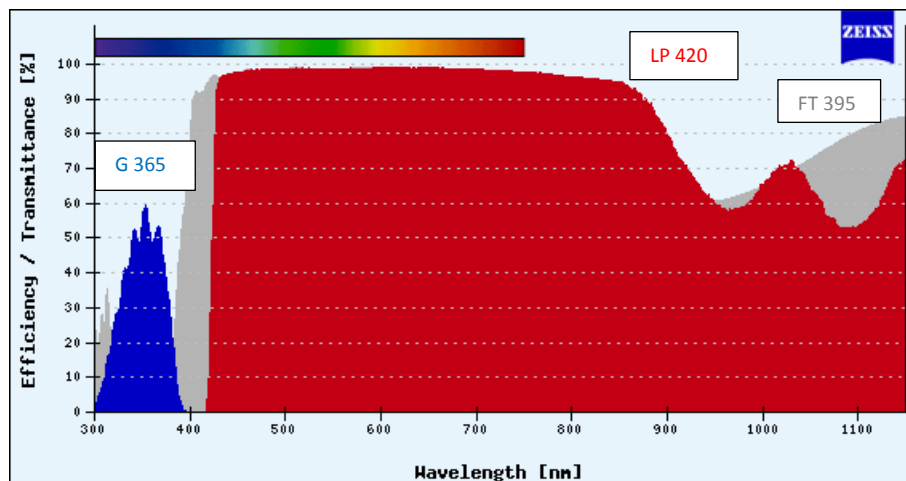


FIGURE1. Specifications for the Zeiss Filter Set 02. As supplied by Zeiss.

Sample preparation: 0.05 micro liter of oil was spread on a microscope slide and covered with a cover slip. No dilutions were required. For comparison purposes and to ensure that there was no UV interference from the slide or coverslip, selected samples were also analyzed in a quartz glass vial as well as a quartz cuvette. There were no significant differences in the fluorescence spectrum as a result of the different type of holders.

### SAMPLES AND PROCEDURE

Fluorescence analyses were carried out on 155 crude oil samples from the Jeanne d'Arc Basin. All crude samples originated either from wellhead or stock tank supplies that had been stored at the CNLOPB storage facility.

Smear slides of oil samples were placed under the Microspectrophotomicroscope. A dark (no optical light) spectral scan was taken to ensure that no stray light entered the system and to provide a background analysis. This was achieved by closing the shutter to the spectrographic head and collecting instrument and optical "noise". The shutter was then opened to collect a sample fluorescence spectrum.

Because of the difficulty in obtaining a universal standard for calibrating the absolute light intensity, relative intensity is used in depicting the fluorescence spectra. All relative energy graphs were normalized to an intensity factor of one for comparison purposes.

### API GRAVITY METHOD

API gravity (that data collected by the authors in the year 2011) were carried out by Petroforma Inc.[15]. They used a Mettler Toledo Densito 10X handheld densometer to measure the density at room temperature, then used the ASTM/API density conversion

## **FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 1 of 2.**

---

table software to convert the density to API gravity at the specified temperature. The authors are unable to account for the method by which the API gravity was collected for the drill stem test in previous years.

### **GASOLINE RANGE AND SATURATE FRACTION GAS CHROMATOGRAMS METHOD**

Gasoline range and saturate fraction gas chromatograms were prepared by the Geological Survey of Canada (Calgary Section). Their method, although published [16], is included below with permission.

#### **PREPARATION OF CRUDE OILS**

About 30-45 ml of oil was poured into a tarred flask, boiling chips were added and the oil was heated up to 210°C. The fraction boiling below 210°C was distilled into a separate flask and weighed. The remaining fraction was cooled and weighed. About 4-5 grams of the fraction boiling above 210°C was deasphalted by adding an excess of pentane (40 volumes). About 100 milligrams of each deasphalted oil were then fractionated using open column liquid chromatography.

#### **ANALYSIS OF GASOLINE FRACTION HYDROCARBONS**

The gasoline range hydrocarbons (iC5-nC8) were analysed on a HP5890 Gas Chromatograph connected to an OI Analytical 4560 purge-and-trap Sample Concentrator. A small amount of the whole crude oil was mixed with deactivated alumina and transferred to the Sample Concentrator which was fitted with a tuna/silica gel/charcoal trap (OI trap #9). This was connected to split/splitless injector on the Gas Chromatograph which was equipped with a 60m x 0.32mm DB-1 column. The initial temperature was held at 30°C for 10 minutes and then programmed to 40°C at a rate of 1°C/min. The final temperature was held for 25 minutes. The eluting hydrocarbons were detected using a flame ionization detector.

#### **LIQUID CHROMATOGRAPHY**

A mixture of 28-200 mesh silica gel (MCB) and 80-200 mesh alumina (ALCOA) (1/3:2/3 by weight respectively) was used as a support for the column. The support is activated by heating at 120°-150°C for 12 hours. A glass wool plug is placed at the bottom of the column and covered with a 1 cm thick layer of sand. The support, weighed as 1 gm of

support/10 mg of deasphalted sample, is slowly settled in pentane and any air trapped is released by gentle tapping on the column. A deasphalted sample, dissolved in a minimal amount of previously measured pentane, is then added to the column. Saturates are recovered by eluting with pentane (3.5 ml/g support), aromatics with a 50:50 mixture of pentane and dichloromethane (4 ml/g support), resins with methanol (4 ml/g support) and any remaining asphaltenes with chloroform. The solvents are rotary-evaporated, separate fractions transferred to tarred 1 dram vials, dried in a slow stream of nitrogen and weighed to constant weight.

#### **GAS CHROMATOGRAPHY**

Saturate fractions were analysed using gas chromatography (GC). A Varian 3700 FID gas chromatograph was used with 30 m DB-1 column with helium as the carrier gas. The temperature programmed was 60°C to 300°C at a rate of 6°C/min and then isothermal for 30 min. The eluting compounds were detected and quantitatively determined using a hydrogen flame ionization detector.

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

**APPENDIX 3**

**FLUORESCENCE SPECTRUM DATA INCLUDING  $\lambda_{\text{max}}$  (in nanometers) AND  $Q_{\text{VALUE}}$  (red/green quotient) AS SHOWN IN THE CRUDE OIL DATABASE**

Fluorescent Information		
MUN Sample Number	$\lambda_{\text{max}}$	Q ratio
Mun0001	574.57	0.74
Mun0002	529.60	0.41
Mun0003	489.32	0.06
Mun0004	438.98	0.08
Mun0005	438.98	0.06
Mun0006	495.70	0.24
Mun0007	495.70	0.26
Mun0008	495.70	0.25
Mun0009	495.70	0.25
Mun0010	527.92	0.34
Mun0011	488.65	0.03
Mun0012	528.26	0.38
Mun0013	527.25	0.35
Mun0014	528.26	0.34
Mun0015	526.91	0.32
Mun0016	528.26	0.34
Mun0017	527.25	0.36
Mun0018	527.58	0.38
Mun0019	492.01	0.06
Mun0020	494.02	0.08
Mun0021	530.61	0.49
Mun0022	528.26	0.35
Mun0023	495.70	0.20
Mun0024	494.02	0.09
Mun0025	438.98	0.04
Mun0026	438.98	0.02
Mun0027	438.98	0.03
Mun0028	528.93	0.34
Mun0029	438.98	0.04
Mun0030	492.35	0.07
Mun0031	489.32	0.04
Mun0032	494.02	0.10
Mun0033	494.02	0.12

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

Fluorescent Information		
MUN Sample Number	$\lambda$ max	Q ratio
Mun0034	495.37	0.14
Mun0036	528.26	0.38
Mun0037	530.61	0.49
Mun0038	530.61	0.49
Mun0039	529.60	0.39
Mun0040	529.60	0.40
Mun0041	528.26	0.35
Mun0042	527.25	0.30
Mun0043	526.91	0.30
Mun0044	529.60	0.41
Mun0045	528.59	0.38
Mun0046	528.59	0.38
Mun0047	530.61	0.44
Mun0048	528.26	0.36
Mun0049	494.36	0.17
Mun0051	529.93	0.40
Mun0052	528.26	0.34
Mun0054	525.24	0.23
Mun0055	527.25	0.33
Mun0056	526.91	0.28
Mun0057	525.24	0.26
Mun0058	438.98	0.02
Mun0059	525.26	0.36
Mun0060	525.57	0.27
Mun0061	526.91	0.31
Mun0062	495.37	0.19
Mun0063	525.24	0.27
Mun0064	495.70	0.24
Mun0065	525.24	0.27
Mun0066	495.70	0.26
Mun0067	495.70	0.20
Mun0068	495.37	0.12
Mun0069	495.70	0.24
Mun0070	530.61	0.45
Mun0071	528.26	0.38
Mun0072	528.26	0.37
Mun0073	496.04	0.26

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

Fluorescent Information		
MUN Sample Number	$\lambda$ max	Q ratio
Mun0074	525.24	0.26
Mun0075	527.92	0.36
Mun0076	528.26	0.38
Mun0077	528.26	0.36
Mun0078	528.26	0.37
Mun0079	529.60	0.43
Mun0080	437.30	0.04
Mun0081	492.01	0.10
Mun0082	527.92	0.37
Mun0083	527.25	0.36
Mun0085	526.91	0.32
Mun0086	526.91	0.28
Mun0087	494.36	0.16
Mun0088	489.66	0.06
Mun0089	527.25	0.28
Mun0090	438.98	0.03
Mun0091	528.26	0.40
Mun0092	495.70	0.26
Mun0093	529.60	0.52
Mun0094	526.91	0.31
Mun0095	528.26	0.38
Mun0096	528.26	0.38
Mun0097	528.26	0.38
Mun0098	495.03	0.18
Mun0099	438.98	0.03
Mun0100	489.32	0.03
Mun0101	526.91	0.29
Mun0102	495.70	0.22
Mun0103	438.96	0.05
Mun0104	529.60	0.38
Mun0105	496.04	0.18
Mun0106	437.64	0.03
Mun0107	495.70	0.24
Mun0108	495.37	0.20
Mun0109	496.04	0.24
Mun0110	495.70	0.18
Mun0111	495.70	0.21

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

Fluorescent Information		
MUN Sample Number	$\lambda$ max	Q ratio
Mun0112	495.70	0.18
Mun0113	496.04	0.19
Mun0114	496.04	0.19
Mun0115	496.04	0.18
Mun0116	528.26	0.39
Mun0117	495.37	0.20
Mun0118	495.70	0.17
Mun0119	495.70	0.26
Mun0120	527.25	0.30
Mun0121	526.91	0.31
Mun0122	496.04	0.25
Mun0123	528.26	0.50
Mun0124	526.91	0.33
Mun0126	526.91	0.31
Mun0127	529.60	0.48
Mun0128	529.92	0.31
Mun0129	529.92	0.35
Mun0130	529.92	0.34
Mun0131	525.57	0.33
Mun0132	528.26	0.33
Mun0133	496.04	0.30
Mun0134	573.56	0.79

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

**APPENDIX 4**

**A SELECTION OF MUN SAMPLES WHOSE Q<sub>VALUE</sub> AND API gravity VALUES ARE AS SHOWN IN THE CRUDE OIL DATABASE.**

<b>Data set taken from the Crude Oil Database, where MUN samples have both current and previous API gravity values</b>			
<b>MUN Sample Number</b>	<b>Q<sub>value</sub></b>	<b>Original API<sup>o</sup> (at drill stem test)</b>	<b>Current API<sup>o</sup> (as of yr. 2011)</b>
Mun0002	0.41	31	28.2
Mun0003	0.06	50	44.6
Mun0004	0.08	54	46.2
Mun0005	0.06	58.6	46.6
Mun0006	0.24	31.4	30
Mun0007	0.26	32.6	29.5
Mun0008	0.25	32.8	29.4
Mun0009	0.25	32.3	31.3
Mun0010	0.34	30.1	25.7
Mun0011	0.03	55.9	47.8
Mun0012	0.38	25.6	24.8
Mun0013	0.35	24	24.3
Mun0014	0.34	29.1	28.8
Mun0015	0.32	30.3	28.7
Mun0016	0.34	31.5	27.4
Mun0017	0.36	30.8	26.6
Mun0018	0.38	29.2	25.8
Mun0021	0.49	27	25.1
Mun0022	0.35	26	25.4
Mun0023	0.20	33.6	30.8
Mun0024	0.09	36.1	36
Mun0025	0.04	47.2	45
Mun0026	0.02	48.5	44.6
Mun0027	0.03	52.8	48.7
Mun0028	0.34	34.6	31.8
Mun0029	0.04	53.2	48.1
Mun0030	0.07	37.3	37.2
Mun0032	0.10	42	32.5
Mun0033	0.12	40.7	33.1
Mun0034	0.14	39.4	31.2
Mun0036	0.38	31	23.8
Mun0037	0.49	18.3	17.9
Mun0038	0.49	19	19.2



**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

Data set taken from the Crude Oil Database, where MUN samples have both current and previous API gravity values			
MUN Sample Number	Q <sub>value</sub>	Original API <sup>o</sup> (at drill stem test)	Current API <sup>o</sup> (as of yr. 2011)
Mun0039	0.39	29	23.4
Mun0040	0.40	32.5	25.5
Mun0041	0.35	34.4	26.4
Mun0042	0.30	34.2	26.9
Mun0043	0.30	29.5	27.1
Mun0044	0.41	32	24.3
Mun0045	0.38	30	22.3
Mun0046	0.38	28.7	23.3
Mun0047	0.44	32.2	24.8
Mun0048	0.36	32	24.2
Mun0049	0.17	36	34
Mun0051	0.40	31.3	25.6
Mun0052	0.34	31	25.4
Mun0054	0.23	32.4	29.8
Mun0055	0.33	30.3	25.2
Mun0056	0.28	31.4	30.7
Mun0057	0.26	32.3	28.3
Mun0058	0.02	52.7	43.3
Mun0059	0.36	30	30.7
Mun0060	0.27	28.3	30.5
Mun0062	0.19	32.4	29.3
Mun0063	0.27	33.4	28
Mun0066	0.26	29.7	27.9
Mun0067	0.20	35.6	34.7
Mun0068	0.12	36.3	35.7
Mun0069	0.24	35.3	31.8
Mun0070	0.45	29.2	25.6
Mun0071	0.38	26	23.4
Mun0072	0.37	31.4	25
Mun0073	0.26	31.7	29.4
Mun0074	0.26	29.7	32.4
Mun0075	0.36	31.7	26.4
Mun0076	0.38	30.1	24.5
Mun0077	0.36	31.1	27.2
Mun0078	0.37	31	24.9
Mun0079	0.43	32.2	25.3
Mun0080	0.04	59.3	45
Mun0081	0.10	62.5	43

**FLUORESCENCE MICROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 1 of 2.**

---

Data set taken from the Crude Oil Database, where MUN samples have both current and previous API gravity values			
MUN Sample Number	Q <sub>value</sub>	Original API <sup>o</sup> (at drill stem test)	Current API <sup>o</sup> (as of yr. 2011)
Mun0082	0.37	30.5	25.4
Mun0085	0.32	32.6	26.2
Mun0086	0.28	33.7	27.9
Mun0087	0.16	34.7	34.2
Mun0088	0.06	58.7	46.4
Mun0089	0.28	32	25.3
Mun0090	0.03	56.6	45.2
Mun0091	0.40	22.8	19.3
Mun0092	0.26	28.1	25.7
Mun0093	0.52	20.5	18.1
Mun0094	0.31	21.6	20.7
Mun0095	0.38	23.8	21.1
Mun0096	0.38	29	24.6
Mun0097	0.38	33.9	29.3
Mun0098	0.18	34.1	29.4
Mun0099	0.03	51.8	44.5
Mun0100	0.03	54	42.7
Mun0101	0.29	30.5	26.7
Mun0102	0.22	32	28
Mun0103	0.05	54.1	44.4
Mun0105	0.18	33	32.2
Mun0106	0.03	53.4	44.9
Mun0107	0.24	34.8	28
Mun0108	0.20	36.2	29.2
Mun0109	0.24	35.5	28.3
Mun0110	0.18	34	31.5
Mun0111	0.21	33.1	30.1
Mun0112	0.18	34	31.8
Mun0113	0.19	33.6	31.2
Mun0114	0.19	33.8	31.9
Mun0115	0.18	34	31.8
Mun0117	0.20	33	29.5
Mun0118	0.17	30.2	30.8
Mun0119	0.26	31.5	29
Mun0120	0.30	20.1	19.6
Mun0124	0.33	24	21.4

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

**PART 2 of 2: Electronic Files**

**C O D a CRUDE OIL DATABASE**

Helen Gillespie<sup>a</sup>, Elliott Burden<sup>b</sup>, and Kirk Osadetz<sup>c</sup>.

a) Research Laboratory Co-ordinator, CREAT Network, Memorial University of Newfoundland.

b) Professor, Department of Earth Science, Memorial University of Newfoundland.

c) Head of Energy Geoscience Subdivision, Geological Survey of Canada, Calgary.

A Report Prepared for the Province of Newfoundland and Labrador Petroleum Exploration Enhancement Program (PEEP).

Date: November 30, 2012

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources, Part 2 of 2**

---

	Page
<b>TABLE of CONTENTS</b>	
Introduction.....	01
Opening USB drive.....	01
Contents of the USB folders.....	01
Starting ACCESS and opening the database.....	02
Explanation of the Database Objects.....	02
Tables.....	02
Records.....	05
Fields.....	05
Relationships.....	07
Queries.....	08
Forms.....	09
Reports.....	11
Summary.....	11
Limitations of the data.....	11
Reference.....	12

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---



## **C O D a CRUDE OIL DATABASE**

### **INTRODUCTION**

The Crude Oil Database (C O D) provides physical and geochemical information on 155 crude oil samples from Newfoundland and Labrador. This information is of use to individuals, companies or institutions that conduct basin analysis studies whether they are examining crude oil, organic rich sediments or petroleum fluid inclusions.

### **OPENING USB DRIVE**

Open the USB flash drive provided with this report to see its contents.

There are five folders (FIGURE 1).

Name	Date modified	Type	Size
USB	04/10/2012 2:39 PM	File folder	
Raw Data folder	04/10/2012 2:37 PM	File folder	
Peep Report folder	04/10/2012 2:37 PM	File folder	
Geochemistry Information folder	04/10/2012 2:36 PM	File folder	
Fluorescence Information folder	04/10/2012 2:36 PM	File folder	
COD Database folder	04/10/2012 2:35 PM	File folder	

FIGURE 1: Contents of the USB flash drive.

### **CONTENTS OF THE FOLDERS**

The COD Database folder contains the Crude Oil Database. This database is opened with the program **Microsoft Office® Access™ 2007**. For the database to operate properly all files must remain in their assigned folders. Removal of files can corrupt the operation of the database. It is recommended that all files be copied to another location, or archived, prior to their use.

The Fluorescence Information folder contains .pdf files of fluorescence spectrograms. It is linked to the Crude Oil Database by way of attachments.

The Geochemistry Information folder contains .pdf and .txt files of geochemistry spectrograms and their reports. These files are linked to the Crude Oil Database by way of attachments.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

---

The Raw Data folder contains a Microsoft Excel workbook of the fluorescent data. One sheet in the book contains the unprocessed original fluorescence spectrum data that has been collected by Memorial University's CREAT Network Laboratory; the second sheet contains the same data in a normalized format. The raw data is provided as a deliverable in the event that a user wishes to see or use the raw fluorescence data of specific oil samples.

The Peep Report folder contains a copy of the written report that you are currently reading.

### STARTING MICROSOFT ACCESS AND OPENING THE DATABASE

Opening the database requires **Microsoft Office Access 2007**.

In **ACCESS**, the database consists of a collection of tables and forms, each of which has information on specific subjects (**TABLES**) or allows the user to enter information on specific subjects (**FORMS**). The difference between storing the data in a spreadsheet and storing it in a database lies in how the data is organized in specific tables. In a database the data is organized in a manner that eliminates duplication.

Start the **ACCESS** program on your computer. From the COD Database folder open the Crude Oil Database file. To the left of the screen there is a **Navigation Plane** if it is not open click the shutter button [ >> ] in the upper left corner to expand its contents. **ACCESS** Objects listed in this navigation pane include a list of all Tables, Queries, Forms and Reports found in the Crude Oil Database (FIGURE 2).

### EXPLANATION OF THE DATABASE OBJECTS

#### TABLES

The Crude Oil Database file has 6-tables (FIGURE 3a-3f) of information on crude oil samples. These include: an API Gravity Information table, a Fluorescence Information table, a Geochemistry Information (after 2011) table, a Geochemistry Information (prior to 2011) table, a Sample Information table and a Well Location table.

The API Gravity Information table (FIGURE 3a) lists the oils specific gravity. The Fluorescence Information table (FIGURE 3b) contains records on the oils fluorescence. The Geochemistry Information tables (FIGURE 3c, 3d) contains reports on the oils geochemistry. The Sample Information table contains identification information for each oil sample (FIGURE 3e). The Well Location table (FIGURE 3f) contains geographical information about where the oil wells were drilled.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

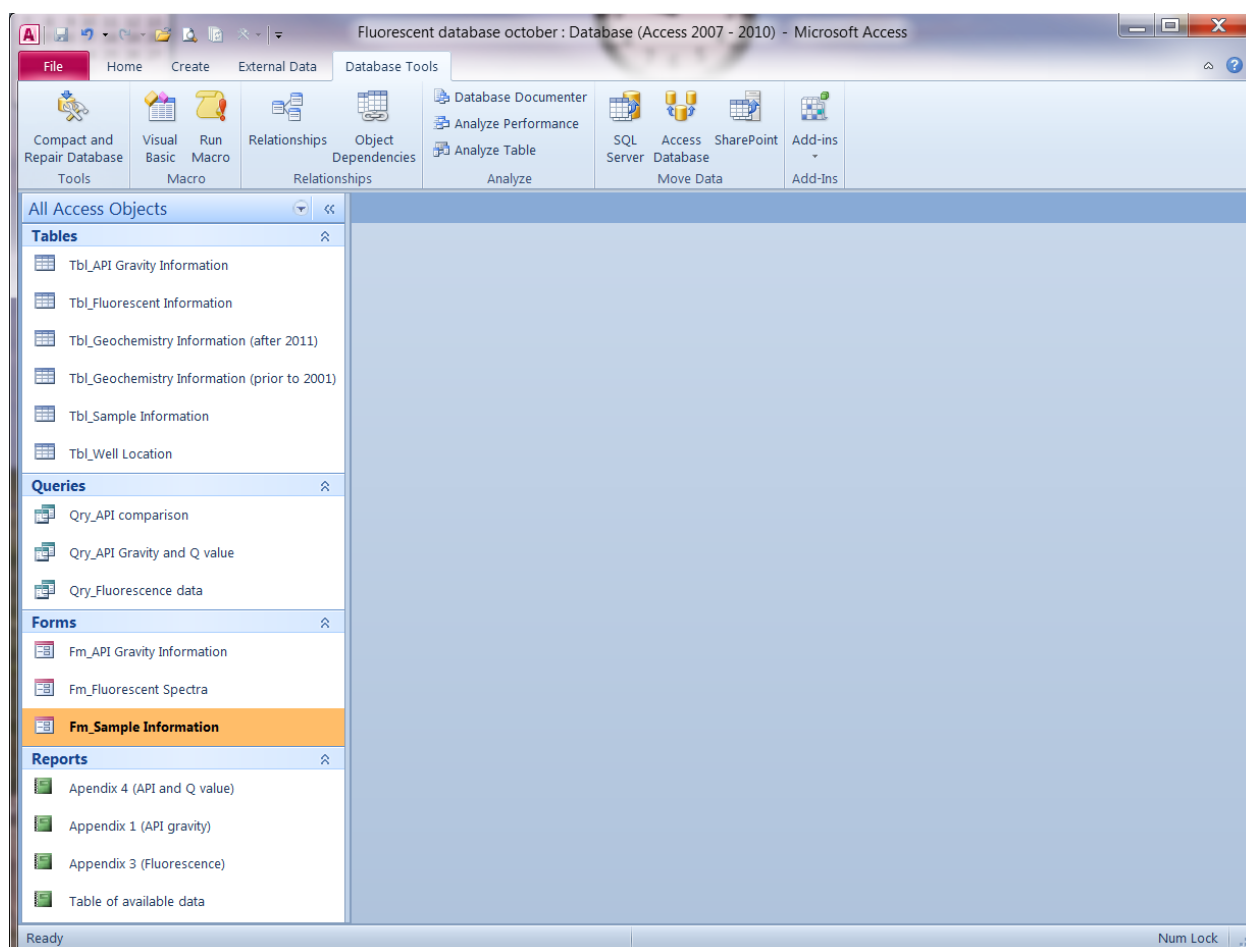


FIGURE 2: Illustration of all Access Objects.

To open any given table, point to that table and double click or use Open in the drop down menu. The table window will appear as outlined below although the order in which the fields (vertical columns) appear may vary and column widths may be truncated as space permits. Expand or unhide the columns to read the **FIELD** names.

Tbl_API Gravity Information							
API ID	MUN ID	Extract type	DST sampling date	DST API (1972-2000)	MUN sampling date	MUN API (2011) at 15	
170	Mun0001	oil	06-Aug-72	6.7			
171	Mun0002	oil	27-Jul-73	31		28.2	
3	Mun0003	condensate	14-Jul-74	50	05-May-11	44.6	
4	Mun0004	condensate	28-Jul-75	54	05-May-11	46.2	
5	Mun0005	condensate	09-Aug-78	58.6	05-May-11	46.6	

FIGURE 3a: API Gravity table.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR

### Department of Natural Resources, Part 2 of 2

Tbl_Fluorescent Information						
	Fluorescent ID	MUN ID	λ max	Q ratio	Fluorescence Graph	Click to Add
+	1	Mun0001	574.57	0.74	0(1)	
+	68	Mun0002	529.60	0.41	0(1)	
+	79	Mun0003	489.32	0.06	0(1)	
+	90	Mun0004	438.98	0.08	0(1)	
+	101	Mun0005	438.98	0.06	0(1)	

FIGURE 3b: Fluorescence Information table.

Tbl_Geochemistry Information (after 2011)										
MUN ID	GSC's sample #	Percent Hydr	Percent Resins an	Percent Satur	Percent Arom	GRGC graph	GRGC report	SFGC graph	SFGC report	Date collected
Mun0004	L00097a	76.53	0.74	69.81	6.72	0(1)	0(1)	0(1)	0(1)	05-Jan-12
Mun0001	L00124a	44.77	49.87	7.47	37	0(1)	0(1)	0(1)	0(1)	21-Dec-11
Mun0005	L00143a	88.61	0.45	81.57	7.04	0(1)	0(1)	0(1)	0(1)	21-Dec-11
Mun0006	L00145a	86.02	11.54	59.62	26.41	0(1)	0(1)	0(1)	0(1)	21-Dec-11
Mun0009	L00151a	85.03	8.8	60.36	24.67	0(1)	0(1)	0(1)	0(1)	22-Dec-11

FIGURE 3c: Geochemistry Information table (after 2011).

Tbl_Geochemistry Information (prior to 2001)											
Geochem ID ▾	MUN ID ▾	GSC's sample # ▾	Percent Hydroc ▾	Percent Resins a ▾	Percent Saturates ▾	Percent Arom ▾	GRGC graph	GRGC report	SFGC graph	SFGC report	Date collector ▾
2	Mun0001	L00124	50.25	11.77	12.3	37.95	0(0)	0(0)	0(1)	0(1)	12-Mar-01
3	Mun0002	L00125	87.3	11.45	56.26	31.04	0(0)	0(0)	0(1)	0(1)	12-Mar-01
1	Mun0004	L00097	95.32	0.53	82.09	13.23	0(0)	0(0)	0(0)	0(0)	
4	Mun0005	L00143	94.1	2.29	84.6	9.5	0(0)	0(0)	0(0)	0(0)	
69	Mun0006	L00389					0(1)	0(1)	0(0)	0(0)	01-Mar-01
70	Mun0007	L00390					0(1)	0(1)	0(0)	0(0)	01-Mar-01

FIGURE 3d: Geochemistry Information table (prior to 2001).

Tbl_Sample Information									
MUN ID	Well Name	Top of Interval	Bottom of Interval	Formation Name	Member Name	DST	Zone	Supplied by	Click to Add
Mun0001	Hibernia B-08	2293	2305.8	Dawson Canyon	Petrel Member	6	4	CNLOPB	
Mun0002	Adolphus 2K-41	2609.1	2647.2	Eider	Petrel Member	3		CNLOPB	
Mun0003	Gudrid H-55	2663.4	2723.1	unknown		2		CNLOPB	
Mun0004	Snorri J-90	2493.3	2502.4	Cartwright	Upper Gudrid	1		CNLOPB	
Mun0005	Hopedale E-33	1938	1997	Bjarni		1		CNLOPB	

FIGURE 3e: Sample Information table.

Tbl_Well Location							
Well Name	UWI	CNLOPB Well Number	Type of Well	Area	Latitude	Longitude	
Bjarni O-82	300O825540057300	63	Delineation	LAB	55° 31' 48.45 "	57° 42' 30.99 "	
Gudrid H-55	300H555500055450	40	Exploration	LAB	54° 54' 30.19 "	55° 52' 28.47 "	
Hopedale E-33	300E335600058451	56	Exploration	LAB	55° 52' 24.62 "	58° 50' 48.78 "	
Snorri J-90	300J905720059450	47	Exploration	LAB	57° 19' 44.92 "	59° 57' 40.74 "	
Ben Nevis L-55	300L554640048150	164	Delineation	NGB	46° 34' 34.59 "	48° 23' 44.53 "	

FIGURE 3f: Well Location table.

## FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

---

### RECORDS

The rows in each of the tables are referred to as **RECORDS**. A record will contain information about a specific oil sample or a specific well as identified in the table. For example the first row in the Sample Information table will contain information on oil sample number Mun0001 under the following **FIELDS**: Well Name, Formation Name, Member Name etc.

### FIELDS

The columns in the tables are referred to as **FIELDS**. A field contains a specific piece of information within a record. In the Sample Information table the fifth field, Formation Name, shows the name of the rock unit from which an oil sample was taken.

The first field in the Sample Information table is the Memorial University of Newfoundland's (MUN's) Sample Number or MUN ID. Memorial University's CREAT Network Laboratory has assigned a number to each sample for identification purposes. It consists of three letters (Mun) followed by a four digit number (0001).

These MUN Numbers are unique in that no two samples are assigned the same number. If there are two or more oil samples from the same location that have different collection dates or were provided to Memorial by a different supplier then those oils are treated as different samples and given unique MUN ID's. The **MUN ID** field in this instance is also used as a **UNIQUE IDENTIFIER**. This simply means that a given sample number can only appear as a single record in this particular table. This unique identifier is also known as a **PRIMARY KEY**. Thus, in this instance the MUN ID is the primary key for the Sample Information table. Other tables have their own assigned primary keys.

All **TABLES** in this database have several fields containing specific sample information relevant to that table. These tables and their fields are listed below.

The API Gravity Information table contains seven fields (FIGURE 3a):

API Gravity ID (auto numbering for each sample entered into this table); MUN ID (CREAIT Network's sample identification); Extract type (whether it is oil or condensate etc.); DST sampling date (drill stem test date for original API gravity); DST API Gravity (1972-2000) (this is the API gravity at the time of the DST); MUN sampling date (the date in which MUN's API gravity was collected); and MUN API Gravity (2011) at 15° (this is the API gravity of the sample when collected in 2011).

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

---

The Fluorescence Information table contains five fields (FIGURE 3b):

Fluorescent ID (auto numbering for each sample entered into this table); MUN ID (CREAIT Network's sample identification) ;  $\lambda_{\max}$  (wavelength of maximum intensity);  $Q_{\text{value}}$  (is the ratio in intensity of the red 650nm wavelength to the green 500nm wavelength); and a Fluorescence Graph (an attachment of the fluorescence spectrum). All data was collected in 2011 and 2012.

The Geochemistry Information (after 2011) table contains eleven fields (FIGURE 3c):

Geochem ID (auto numbering for each sample entered into this table); MUN ID (CREAIT Network's sample identification); GSC Sample Number (the Geological Survey of Canada's sample identification); Percent Hydrocarbons (this includes the weight percent of both saturates and aromatics); Percent Resins (weight percent of resins); Percent Saturates (weight percent of saturates); Percent Aromatics (weight percent aromatics); C5-C8 Graph (gasoline fraction gas chromatograph graph); C5-C8 Report (gasoline fraction gas chromatograph report); C10-C32 Graph (saturated fraction gas chromatograph graph); and C10-C32 Report (saturated fraction gas chromatograph report). Date collected (this is a general date on which the data was collected) for specific dates the reader is referred to the date that is provided inside the attached reports.

The Geochemistry Information (prior to 2001) table contains eleven fields (FIGURE 3d):

Geochem ID (auto numbering for each sample entered into this table); MUN ID (CREAIT Network's sample identification); GSC Sample Number (Geological Survey of Canada's sample identification); Percent Hydrocarbons (this includes the weight percent of both saturates and aromatics); Percent Resins (weight percent of resins); Percent Saturates (weight percent of saturates); Percent Aromatics (weight percent aromatics); C5-C8 Graph (gasoline fraction gas chromatograph graph); C5-C8 Report (gasoline fraction gas chromatograph report); C10-C32 Graph (saturated fraction gas chromatograph graph); C10-C32 Report (saturated fraction gas chromatograph report). Date collected (this is a general date on which the data was collected) for specific dates the reader is referred to the date that is provided inside the attached reports.

The Sample Information table contains nine fields (FIGURE 3e):

MUN ID (CREAIT Network's sample identification); Well Name (name of the well from which the sample was collected); Top of Well Interval (top of the sampling interval, in meters); Bottom of Well Interval (bottom of the sampling interval, in meters); Formation Name (geological formation from which the sample was collected); Member Name (geological member of the formation from which the sample was collected); DST (drill

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

stem test); Zone (zone from which sample was collected); and Supplier (organization that provided the sample).

The Well location table contains seven fields (FIGURE 3f):

Well Name (name of the well as assigned by the exploration company); UWI (Canada-Newfoundland and Labrador Offshore Petroleum Board's (CNLOPB's) unique well identifier); CNLOPB Well Number (well number assigned by CNLOPB, in the order of drilling); Type of well (classification of well during drilling); Area (geographic location); Latitude (surface co-ordinate); and Longitude (surface co-ordinate).

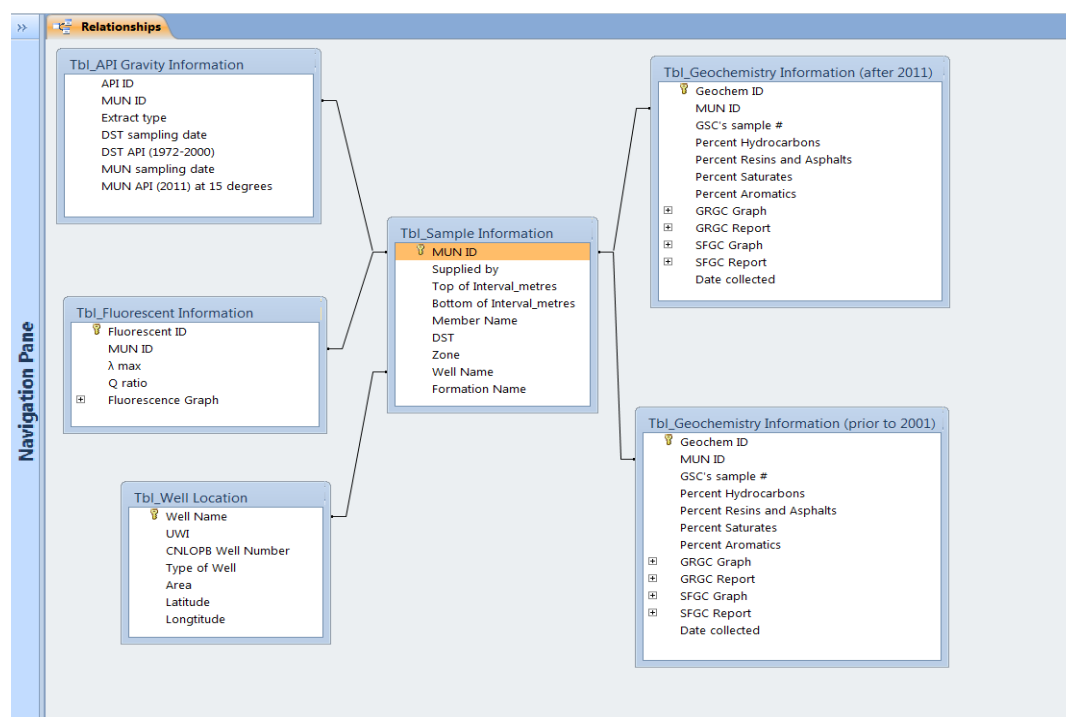


FIGURE 4: Table Relationships (links between different tables).

## RELATIONSHIPS

All six tables are linked according to the relationship diagram (FIGURE 4). All tables are linked by a common field, either the MUN ID or by the Well Name. For those familiar with Microsoft Access this linkage will let the user ask complex questions by using **QUERIES** or assist in producing **FORMS** and **REPORTS** as part of the Microsoft Access database software.



## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

### QUERIES

**QUERIES** are used to extract subsets of data from one or more tables. The data that you require may be stored in one or more tables and a query lets you view data from several tables in a single datasheet. A query retrieves data and makes it available for use. How to make queries is not within the scope of this report but it is important to know the versatility of the Microsoft Access Program.

There are three **QUERIES** included in this report. FIGURE 5a illustrates an API Gravity comparison query where the drill stem test API gravity can be compared to that of MUN's API gravity. That data is sorted in descending order with respects to MUN API Gravity data. The second, FIGURE 5b, is a Fluorescence data query which contains information with regard to samples fluorescence and its data has been sorted by Well Name. The third query, FIGURE 5c, is the API Gravity and  $Q_{\text{value}}$  query which contains information on the sample API gravity as well as the fluorescence  $Q_{\text{value}}$ . This data has been sorted by MUN ID. These queries provided the data in which **REPORTS** were created.

Qry_API comparison				
MUN ID	Well Name	Top of Interval_metres	DST API (1972-2000)	MUN API (2011) at 15
Mun0027	Hibernia B-08	3018	52.8	48.7
Mun0029	Hibernia B-08	2954	53.2	48.1
Mun0011	Bjarni O-82	2362	55.9	47.8
Mun0005	Hopedale E-33	1938	58.6	46.6
Mun0088	South Mara C-13	2926.1	58.7	46.4

FIGURE 5a: Illustrates an API Gravity comparison query for various MUN samples which included Well Name, Top of well interval, Drill Stem test API and MUN API.

Qry_Fluorescence data				
MUN ID	Well Name	Top of Interval_	$\lambda$ max	Q ratio
Mun0002	Adolphus 2K-41	2609.1	529.60	0.41
Mun0019	Ben Nevis I-45	2883.4	492.01	0.06
Mun0020	Ben Nevis I-45	4426.1	494.02	0.08
Mun0021	Ben Nevis I-45	2440.6	530.61	0.49
Mun0142	Ben Nevis I-45	2420.1	526.91	0.29

FIGURE 5b: Illustrates a Fluorescence data query for various MUN samples which included Well Name, Top of well interval,  $\lambda$  max and Q ratio.



## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

Qry_API Gravity and Q value				
MUN ID	DST API (1972-2000)	MUN API (2011) at 15	Q ratio	
Mun0001	6.7		0.74	
Mun0002	31	28.2	0.41	
Mun0003	50	44.6	0.06	
Mun0004	54	46.2	0.08	
Mun0005	58.6	46.6	0.06	

FIGURE 5c: Illustrates an API Gravity and Q<sub>ratio</sub> query.

### FORMS

There are three forms included in this database: an API Gravity Information form; a Fluorescence Spectra Information form; and a Sample Information form (FIGURE 6a, 6b, 6c). They are included in this report to allow the user to see the versatility of the Microsoft Access Program.

These forms were created as data entry screens. They are the interfaces that you would normally use when working with data, and they often contain elements and command buttons that make data entry and performing various tasks quick and easy.

You may update this database (add, change or delete) without using forms by simply editing the data in the table datasheets. **However this is not recommended.** Before modifying the data one should make a copy of the database. Once data is deleted it cannot be recovered. Memorial University, CREAT Network will have a backup of this report in the event of such problems.

Fm_API Gravity Information						
API Gravity Information						
API ID	<input type="text" value="170"/>	DST sampling date	<input type="text" value="06-Aug-72"/>			
MUN ID	<input type="text" value="Mun0001"/>	DST API (1972-2000)	<input type="text" value="6.7"/>			
Extract type	<input type="text" value="oil"/>	MUN sampling date	<input type="text"/>			
		MUN API (2011) at 15 degrees	<input type="text"/>			

API ID	MUN ID	Extract type	DST sampling date	DST API (1972-2000)	MUN sampling date	MUN API (2011) at 15
170	Mun0001	oil	06-Aug-72	6.7		
171	Mun0002	oil	27-Jul-73	31	05-May-11	28.2
3	Mun0003	condensate	14-Jul-74	50	05-May-11	44.6

FIGURE 6a: API Gravity Information form.

## FLUORESCENCE MICROSCPECTROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

Fm\_Fluorescent Spectra

### Fluorescent Spectra

MUN ID

λ max

Q ratio

Fluorescence Graph

MUN ID	λ max	Q ratio	
Mun0001	574.57	0.74	(1)
Mun0002	529.60	0.41	(1)
Mun0003	489.32	0.06	(1)
Mun0004	438.98	0.08	(1)

FIGURE 6b: Fluorescence Information form.

Fm\_Sample Information

### Sample Information

MUN ID

DST

Supplied by

Zone

Top of Interval\_metres

Well Name

Bottom of Interval\_metres

Formation Name

Member Name

MUN ID	Supplied by	Top of Interval	Bottom of Interv	Member Name	DST	Zone	Well Name	Formation Name
Mun0001	CNLOPB	2293	2305.8	Petrel Member	6	4	Hibernia B-08	Dawson Canyon
Mun0002	CNLOPB	2609.1	2647.2	Petrel Member	3		Adolphus 2K-41	Eider
Mun0003	CNLOPB	2663.4	2723.1		2		Gudrid H-55	unknown
Mun0004	CNLOPB	2493.3	2502.4	Upper Gudrid	1		Snorri J-90	Cartwright

FIGURE 6c: Sample Information form.

## **REPORTS**

You can use reports to print and summarize data that are available in the various tables, forms or queries. Three reports have been generated in the Crude Oil Database.

Here three reports are created from previously selected data that has been generated using the QUERIES listed in the database. Appendix 1 is a report that compares the DST API Gravity (which was collected at the time of drilling) to the API Gravity collected in (2011-2012); Appendix 3 is a report which contains selected fluorescence data that has been sorted by  $\lambda_{\max}$ ; and Appendix 4 contains information which illustrates the relationship between API gravity and  $Q_{\text{value}}$  data. These three reports are included as Appendices in Part 1 of this report.

Before printing, reports can be viewed on screen, exported to another application or sent via email as an attachment or a message.

## **SUMMARY**

In summary the Crude Oil Database is a very functional database which contains information on crude oil samples. The information includes: Well and Sample information in addition to API Gravity, Geochemistry and Fluorescence data. The Crude Oil Database runs in **Microsoft Office® Access™**. Its files can be easily downloaded unto a desktop computer or be incorporated into a pre-existing database.

The data can be useful to anyone involved in oil related studies.

### **Limitations of the data**

Limitations to the use of the data contained in this database are addressed in Part 2 of this report. The reader is also referred to the section on Source and Conditions on Geochemistry Information disclaimer located at the front of this report.

**NOTE:** When using or comparing information from this database, users should observe the date and experimental conditions in which that information was originally collected. Various types of analyses were carried out on different dates under different circumstances. All analytical methods used to collect data are included in Appendix 2, Part 1, of this report.

## FLUORESCENCE MICROSCOPY REPORT FOR Department of Natural Resources, Part 2 of 2

---

### REFERENCE

#### RESOURCE USE IN the WRITING THIS REPORT

Shelly, G. B., Cashman, T.J., Pratt, P. J., and Last, M. Z., 2007. *Introductory Concepts and Techniques*. Shelly Cashman Series Microsoft Office<sup>®</sup> Access<sup>™</sup> 2007. ISBN 13: 978-1-4188-4339-7.

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---

**FLUORESCENCE MICROSPECTROSCOPY REPORT FOR**  
**Department of Natural Resources**

---