

Establishing Crude Oil Concentration in Sediment Applying the Toluene Colour Index Method

By

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Abstract

Seepage crude oil and oil-impregnated sand were sampled in the surroundings of Miri, Sarawak, and mixed/extracted with Toluene in the laboratory. The oil produced a characteristic staining of the Toluene, and it was noticed that the colour of the oil/Toluene mix and oil sand/Toluene extraction appeared to be proportional to the concentration of oil dissolved in the Toluene. The liquid colour changed from faint yellow/green in low concentrations to deep orange, and later at rising oil concentration to orange-brown. Therefore it is concluded that the colour of the Toluene/oil mix can be used to estimate oil saturation (S_o , %) of oil sands, once oil concentrations in Toluene are calibrated with a colour index chart. The method might also be used to quickly assess the amount of crude oil contamination in the aftermath of an oil spill.

Keywords: Oil, Borneo, Miri field, Seepage, Toluene, soil pollution

Introduction

According to data from the Petroleum Museum in Miri, the in 1972 abandoned Miri oil field, situated beneath the city center (Hutchison, 2005 and Fig.1), produced essentially two types of crude: a waxy, free-flowing light crude of some 40 deg Api; a relatively heavy oil, of low wax content and gravity of 20 deg Api in shallow reservoirs was pumped to surface. Oil seepage has been documented in historical time along Quarternary faults, and currently there are two active seep locations. Hence, crude oil in soil is a rather common constituent of the larger Miri area. Soil analysis can be both indicative in the context of oil prospection, and, perhaps even more

important so, in the context of hazard mitigation. A good overview is given by the manual of Petroleum Measurement Standards (1986). In the event of industrial oil spillage affecting soils, it is necessary to assess the extent of contamination. In this article a simple test is described that was developed in the Curtin University, Sarawak, to obtain semi-quantitative oil saturation data in soils, and these at a very low cost.

Miri Oil Seep Locations and Oil Properties

Two accessible seep/oil sand locations were sampled in 2010 and 2011 by the author and Curtin students (Fig.1-4). Oil properties were investigated and are shown in Fig.5. The seepage oil is brown in colour, and offers a penetrating asphaltic smell. GCSM analysis showed that most of the original lighter fraction hydrocarbons are not any longer present.

Sampling and Sample Preparation

Samples from fresh, oil-bearing formation or polluted soils must be packed and transported in pressure-sealed plastic containers. A proper preservation and storage in the lab is of equal importance. If the containers are not properly pressure-sealed, samples tend to dry quickly in the artificially dry air of air-conditioned rooms. Preferably, analysis of the rock or soil samples should be carried out as soon as possible after sampling to avoid a further degradation.

Methodology of Analysis

The analysis is carried out as follows (described in Table 1): a sample, approximately 100 g, in field-wet condition, is split into two sets of 50 g each, samples A and B. Sample A's volume is measured in the following step the sample is dried in the oven at 60 deg C for some 10 hours. After that, both hydrocarbons and water have degassed and escaped. The sample is allowed to cool to room temperature, and its weight is measured. The difference between wet condition weight and dry condition weight equals the former liquid content, both of water and hydrocarbons, and can be used as a measure of connected porosity. Further and more precise porosity and permeability measurements can be applied, permitting laboratory and timing aspects.

Sample B is put in a beaker and sufficient Toluene is added (establish both volume and weight of Toluene ahead of the experiment). In the context of our experiments, Toluene was chosen as a

solvent, given its relatively high boiling point (Table 2). It is an organic compound, liquid at room temperature, formula $C_6H_5CH_3$. It is often used as a solvent for aromatic compounds in liquid chromatography (Miles, 1989).

In the context of Sample B analysis, Toluene should cover the sample by some 1 – 2 centimeters of liquid above sample. Both Sample Band Toluene are left for one hour under room conditions. It is advisable to place the beaker under a fume hood, given that Toluene is considered a toxic and mildly carcinogenic substance. If any oil is present in the sample, it will quickly cause a colour stain in the liquid. Fig. 6 shows Toluene coloured by different concentrations of Miri crude oil.

After one hour of soaking Sample B in Toluene, the liquid is decanted, filtered and measured in weight and volume.

Producing a Colour Calibration Table

Should the oil suspected in the samples under investigation be available as a reference, it is suggested to produce a calibrated oil chart for the specific oil. This is done by preparing four glasses with 5 ml of Toluene in each glass. The crude oil is then added to the Toluene (first glass one drop; second glass, 2 drops; 3rd glass 3 drops etc.). It is important to apply exactly the same quantity of Toluene to each glass.

As the calibration set is ready, the 5 ml of Sample B is compared with the calibration liquids. Given the colour of the sample B is proportional to the amount of oil in the liquid, the amount of the oil concentration can be estimated by comparing sample glass colour to the 'best fit' calibration liquid. An example for a colour table is shown in Fig. 7. In the Miri example, with rising crude oil content, one observes a shift from pale yellow to light green, light orange, and later, with higher concentrations, colours leading to dark orange and finally orange-brown coloration.

With the aid of Table 3 the total oil volume of sample B is computed, and can be compared to the free porosity measurement that was carried out on Sample A. In such ways, an estimate of oil saturation can be obtained.

Additional Measurements

It is suggested to view the Toluene/oil mix under a Ultra-Violet lamp as well. Toluene itself does not produce a strong glow; however the strength of the glow increases rapidly with increasing quantities of crude oil dissolved in Toluene.

Applications and limits of the described method

The method is applicable for the detection, and the semi-quantitative determination of oil saturation in oil sands; the method is particularly well-suited for strongly coloured heavy and/or biodegraded oil, available at low saturations in sand. With rising oil-in-Toluene concentrations (dark orange colours in the Miri case) it becomes increasingly more difficult to establish concentrations. This can be remedied by further diluting the sample with Toluene, until the oil concentration can be better estimated.

The method can also be applied to establish presence and amount of accidentally spilled crude oil in soils. By extracting the oil fraction from soil with Toluene one can assess oil saturation in soil/sediment after a crude oil spillage has occurred.

The method described above works well for heavy oil, and biodegraded oil with long hydrocarbon chains, in particular asphaltenes. The method can also be applied to other hydrocarbons, such as distillates derived from pyrolysis of coal. Toluene coloring does not work well when hydrocarbons are very light (> 35 deg Api), in the very light oil to condensate fraction. The latter tend to be transparent.

Disposal of samples

Toluene when mixed with oil is considered a toxic substance, and needs to be disposed in a responsible way in accordance with the relevant environmental legislation.

Conclusions

The Toluene Colour Index analysis constitutes a cheap, fast and fairly accurate method to check oil saturation in sediments and soils. The method may have its merit when results have to be produced quickly - such as in the aftermath of an industrial oil spill, where every hour counts and relief measures need to be applied promptly. Although other analysis methods (GCMS and other) yield better data of the pollutant, these require a significant amount of sample preparation, such as water removal, and measuring time. The Toluene Colour Index method, however, can be applied directly in the field: rather than bringing oil-stained samples to the laboratory, one might as well bring Toluene samples to the field and carry out oil extraction on the spot. The resulting colour would give a first-order-of-magnitude assessment of oil contamination, and allow a simple mapping of crude oil concentrations in soil. The method might also be used to measure oil saturations in cores; and should be further tested with a variety of crude oils.

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References

American Petroleum Institute (API) 1986. Manual of Petroleum Measurement standards (MPMS), Tulsa, USA.

Hutchison, C.S, 2005. Geology of Borneo, 421 p. Elsevier.

Kessler, F.L.; Jong, J., 2011. Habitat and C-14 age dating of lignitic terrace sands – implications for uplift on the Borneo coastline during the Holocene. PGCE presentation abstracts, Warta Geologi, Vol 37, p. 36.

Lowery, T.H. and Richardson, K.S., 1987. *Mechanism and Theory in Organic Chemistry*, Harper Collins Publishers 3rd ed. 1987

Miles, A.J., 1989. *Illustrated glossary of petroleum geochemistry*, Clarendon Press, Oxford, 237 p.

Petroleum Museum Miri, Miri, Sarawak: <http://www.sarawak-vacation-destinations.com/miri-petroleum-museum.html>

Williams, J., 2000. *Field and laboratory testing of sediment and water in crude oil*. Publ. Savant Measurement Corporation, TX, USA.

Figures

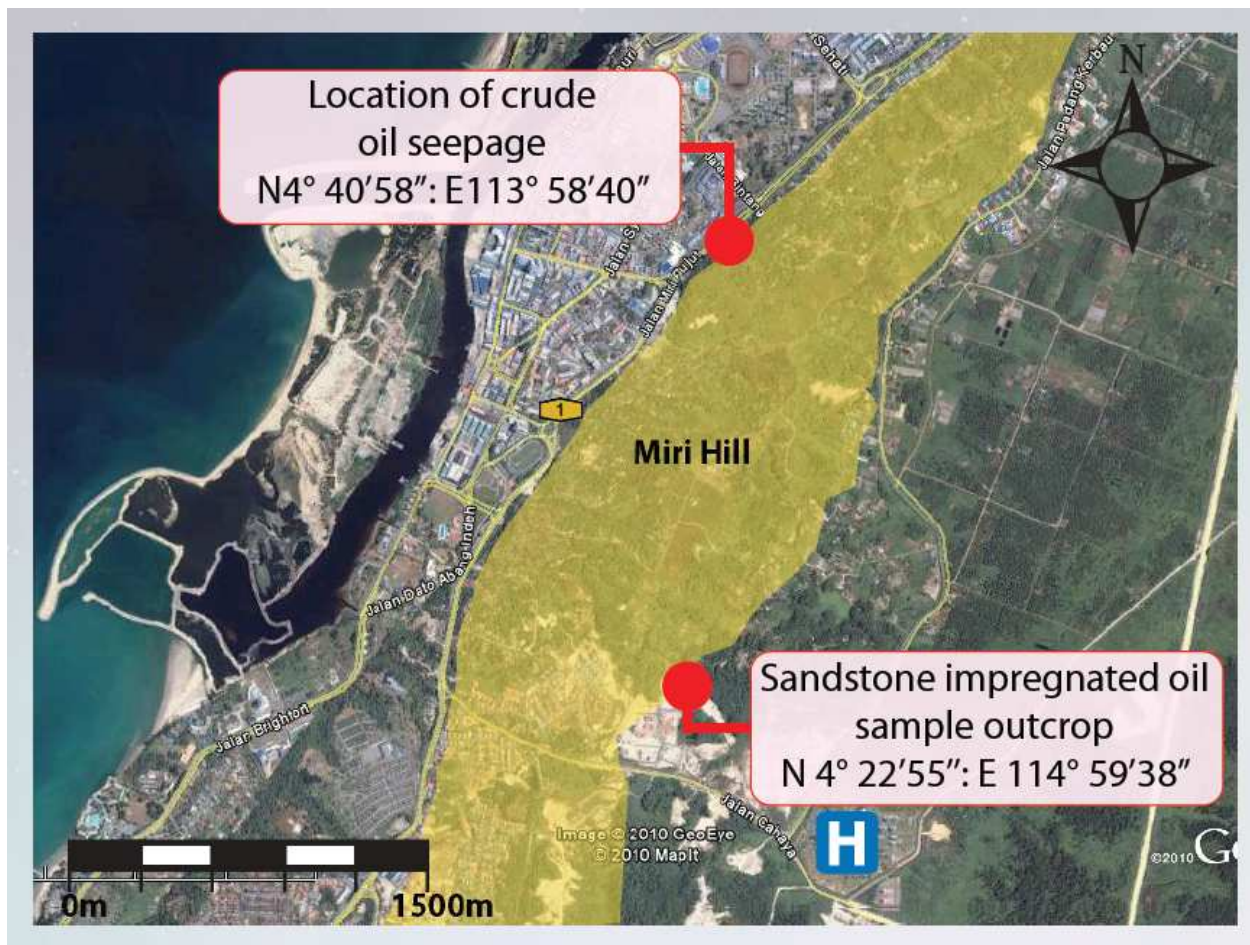


Fig. 1: Map of the Miri area with two major occurrences of seepage: Seep 1 (= sample 1, upper left) is located at the hinge point of a scissor fault; Seep 2 (= sample 2, lower right) is an area in KpgLopeng where oil reservoirs are found at near surface.



Fig. 2: Seep/sample (area 1): Opposite of the Bintang Mall, the seep is located at the hinge point (center of picture) of a complex scissor fault (a normal fault at least in the left side of the picture). Circular fracture systems are seen upwards of the hinge (upper centre left). Most oil oozes from an area right next to the small tree in the centre of the picture. The seepage point was discovered by the author and Curtin students in the aftermath of a tragic landslide event in 2009 that wiped out a Shell filling station and killed two shop workers. The current outcrop surface was created when the landslide surface was cleared from debris, vegetation and soil.



Fig. 3: At the seep location (area 1), oil is seen oozing from the fault plane, more precisely from a sandy- siltyrock wall surrounding the seep area. The oil droplets look greenish, later brownish; oil flow tends to increase after a heavy rain fall.

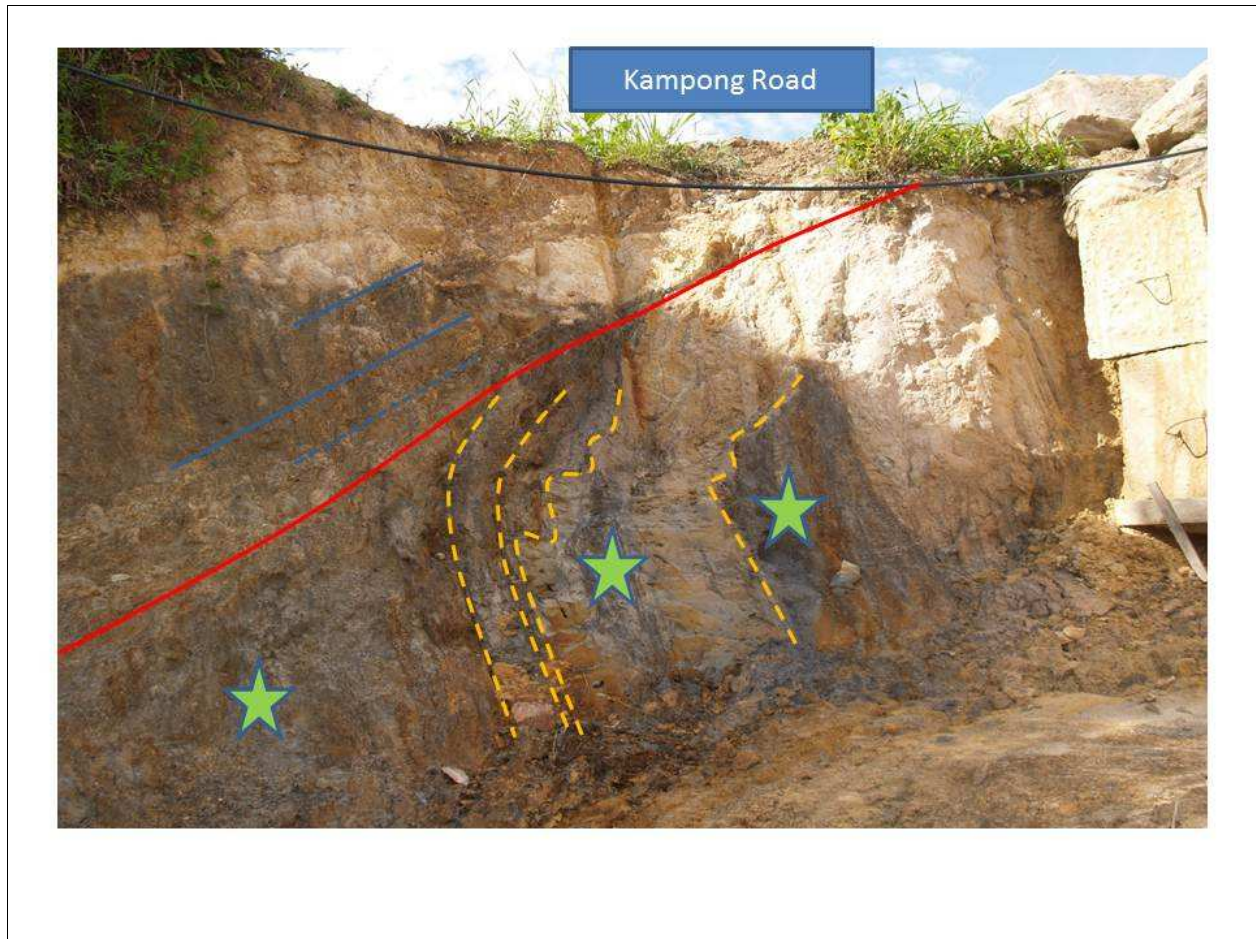


Fig. 4: Outcrops of oil sand strata (stars) in sample area 2. The vertical-bent oil sand layers are seen sub-cropping beneath the Canada Hill overthrust (red). Oil concentration (S_o , %) varies between single digit and double-digit percentage values.

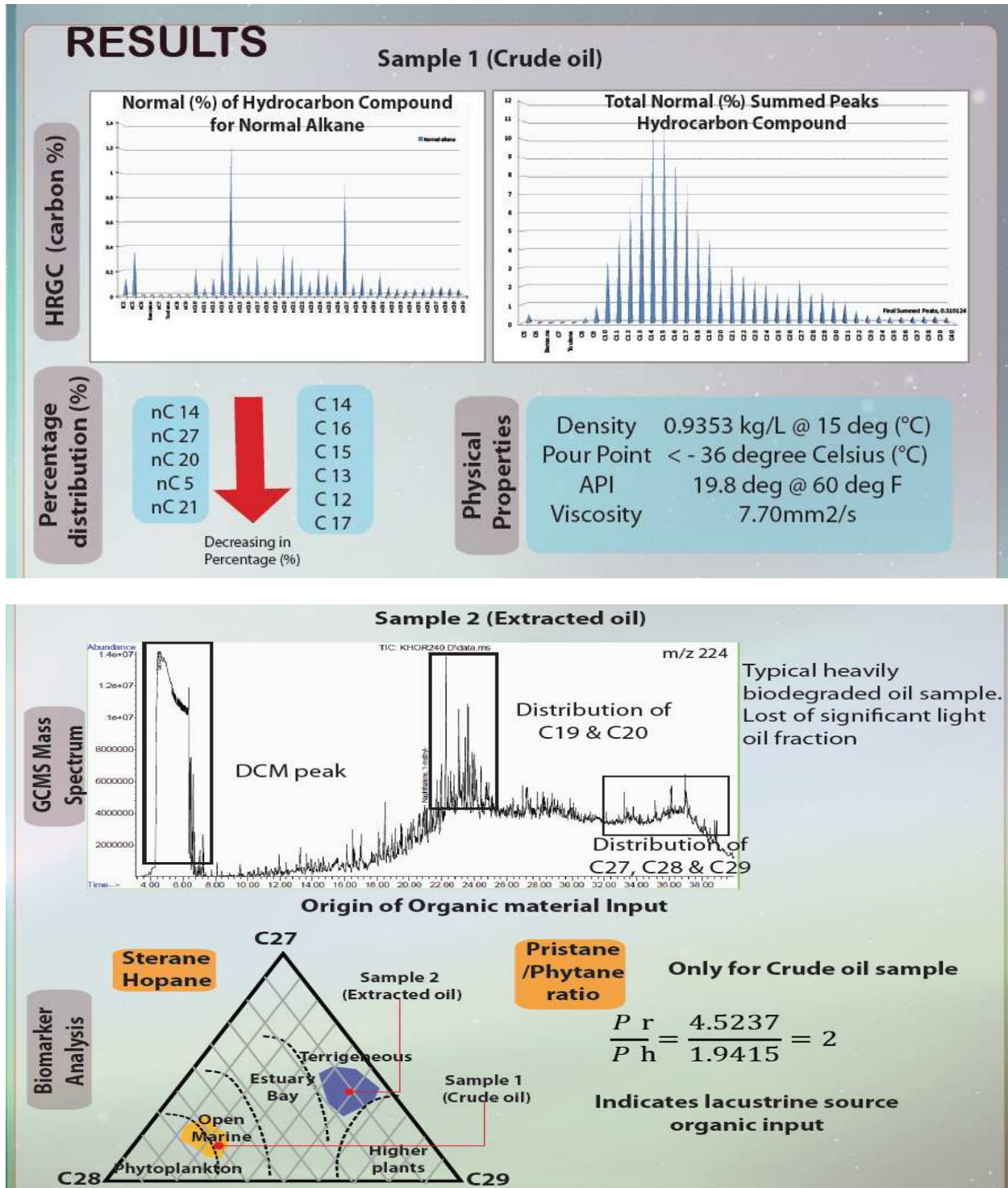


Fig. 5: Both oils from area 1 and 2 are strongly bio-degraded. Older unpublished data by Shell suggest that the bio-degradation took predominantly place before the uplift of the Canada Hill, dated by Kessler & Jong (2011) to be at the boundary between Pleistocene and Holocene or even younger.



Fig. 6: Extractions from oil sands of sample area 2. Two different sand layers containing hydrocarbons were extracted using Toluene. Note the colour difference between the two bottles in the center: faint yellow and dark orange. The latter belongs to a vertical steepened oil sand outcrop, of very strong petroleum smell and sealed by an overthrust fault (shown in Fig. 4). The estimated oil saturation in this sand may be in the order of 20 %. The bottles on either side contain distillate from the oil sands (please note the clear colour, there is little or no oil present in the distillates).

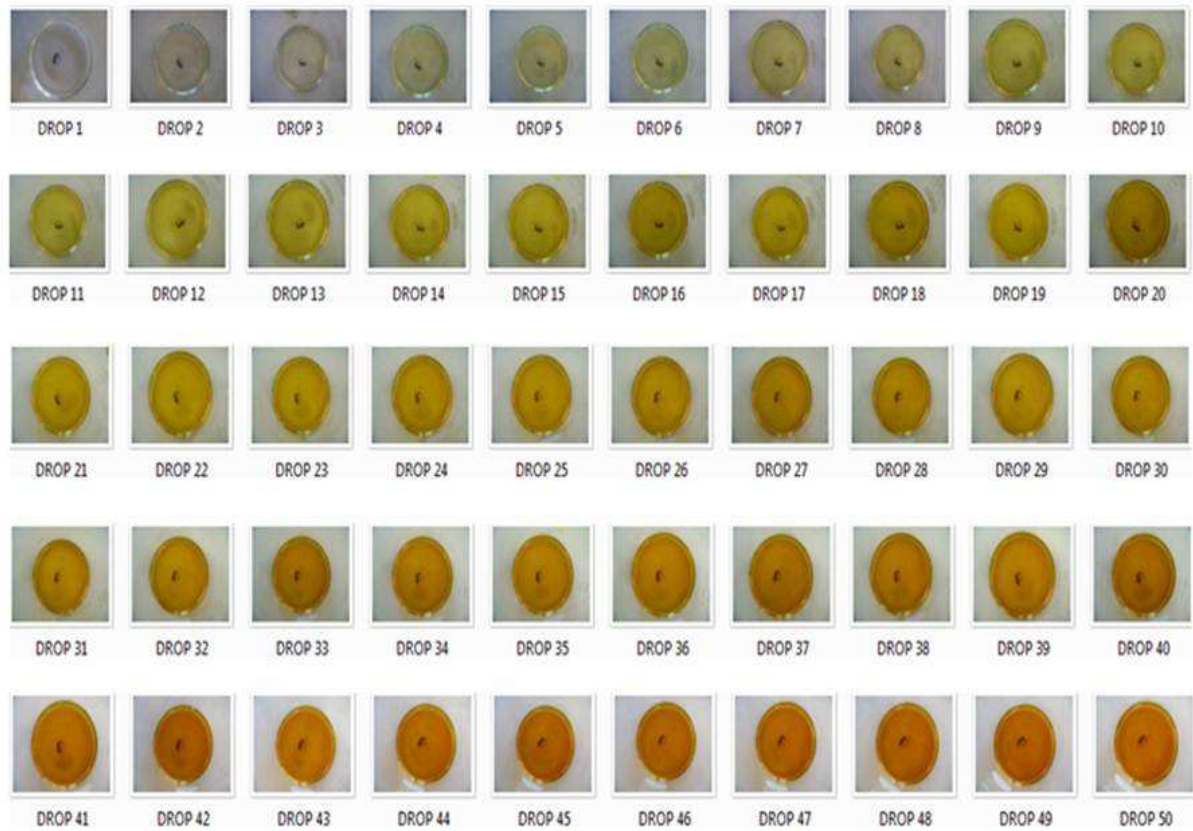


Fig. 7: Colour table for Miri oil from 1 drop per 5 ml Toluene to 50 drops per 5 ml Toluene.

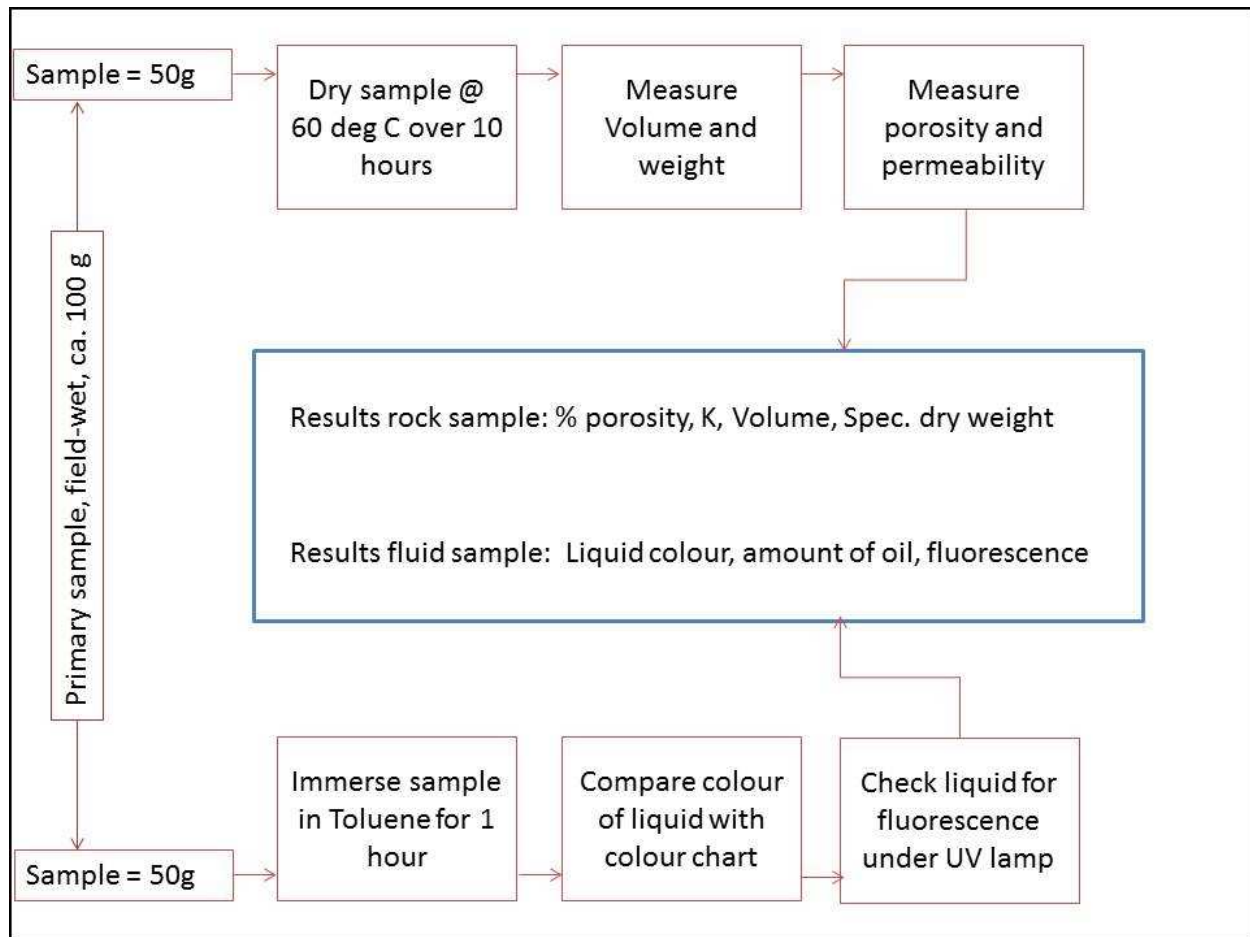


Table 1: Process chart for establishing basic rock and fluid properties

Solvent	Chemical formula	Boiling point ^[7]	Dielectric constant ^[8]	Density	Dipole moment
Non-polar solvents					
Pentane	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃	36 °C	1.84	0.626 g/ml	0.00 D
Cyclopentane	C ₅ H ₁₀	40 °C	1.97	0.751 g/ml	0.00 D
Hexane	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	69 °C	1.88	0.655 g/ml	0.00 D
Cyclohexane	C ₆ H ₁₂	81 °C	2.02	0.779 g/ml	0.00 D
Benzene	C ₆ H ₆	80 °C	2.3	0.879 g/ml	0.00 D
Toluene	C ₆ H ₅ -CH ₃	111 °C	2.38	0.867 g/ml	0.36 D
1,4-Dioxane	<u>/-CH₂-CH₂-O-CH₂-CH₂-O-</u>	101 °C	2.3	1.033 g/ml	0.45 D
Chloroform	CHCl ₃	61 °C	4.81	1.498 g/ml	1.04 D
Diethyl ether	CH ₃ CH ₂ -O-CH ₂ -CH ₃	35 °C	4.3	0.713 g/ml	1.15 D
Polar aprotic solvents					
Dichloromethane (DCM)	CH ₂ Cl ₂	40 °C	9.1	1.3266 g/ml	1.60 D
Tetrahydrofuran (THF)	<u>/-CH₂-CH₂-O-CH₂-CH₂-</u>	66 °C	7.5	0.886 g/ml	1.75 D
Ethyl acetate	CH ₃ -C(=O)-O-CH ₂ -CH ₃	77 °C	6.02	0.894 g/ml	1.78 D
Acetone	CH ₃ -C(=O)-CH ₃	56 °C	21	0.786 g/ml	2.88 D
Dimethylformamide (DMF)	H-C(=O)N(CH ₃) ₂	153 °C	38	0.944 g/ml	3.82 D
Acetonitrile (MeCN)	CH ₃ -C≡N	82 °C	37.5	0.786 g/ml	3.92 D
Dimethyl sulfoxide (DMSO)	CH ₃ -S(=O)-CH ₃	189 °C	46.7	1.092 g/ml	3.96 D

Table 2: Properties of prominent solvents (Lowery et al. 1987). Toluene, Cyclohexane and Benzene are excellent solvents for organic materials, and are, with boiling points above 80 deg C convenient to handle in the laboratory.

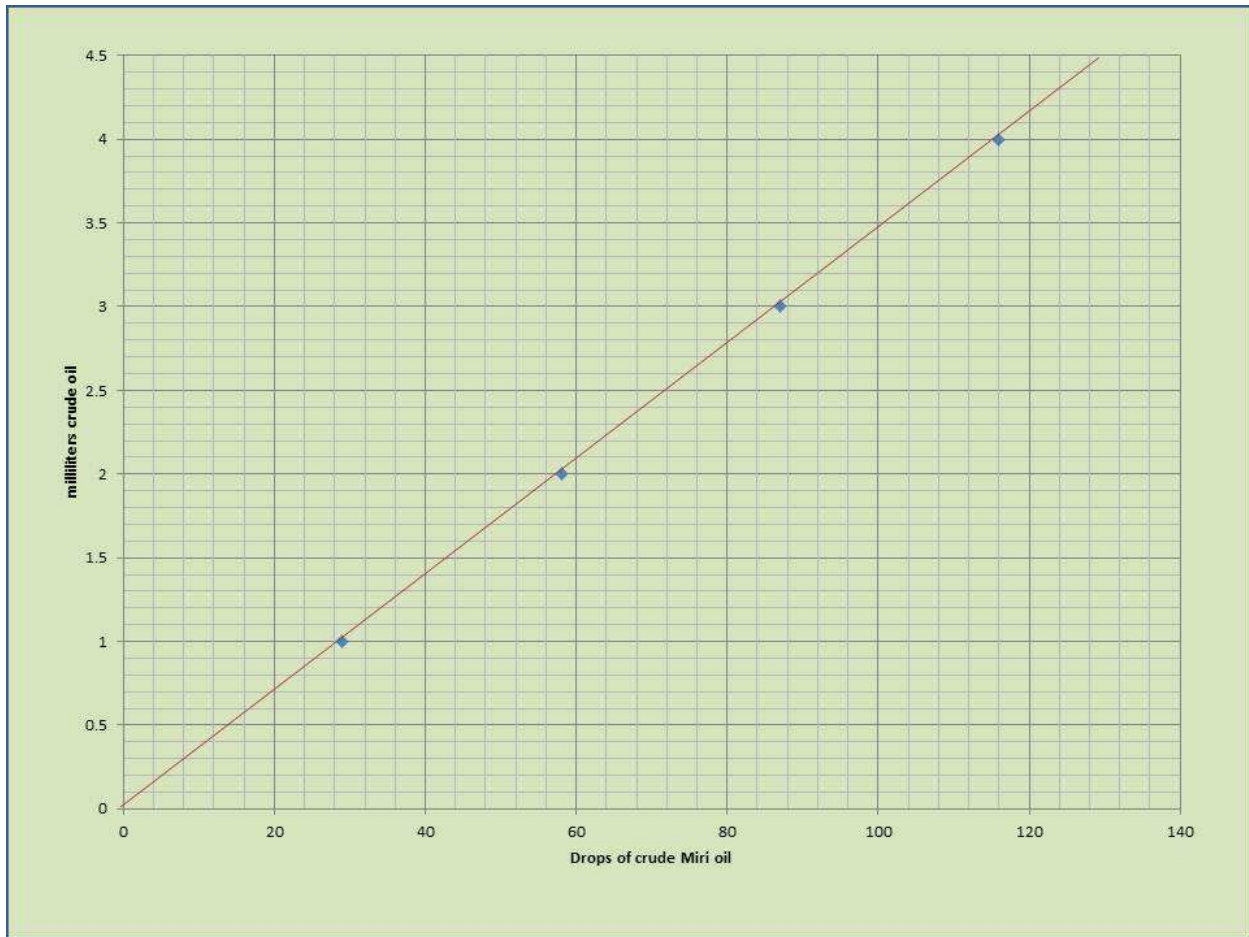


Table 3: Correlation for drops Miri crude oil to volume: 29 drops oil correspond to 1 ml.