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High Temperature Fluorescence Sensor for Oilfield Applications

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Abstract: Optical fluorescence spectra of crude oils depends on the concentrations of certain chemical components, such as asphaltenes, saturates and aromatics present in these oil samples. In this work, we report a high temperature optical fluorescence spectrometer tool for in situ measurements. This instrument uses a miniaturized spectrometer with a small semiconductor laser source and an optical reflection probe. The miniature sensor was controlled with an Arduino Nano device. We have tested our spectrometer to elevated temperatures present in borehole conditions (100 °C). The results indicate that our logging tool will be able to measure ~95 % of our liquid wells. The fluorescence measurements were compared to standard Saturates-Aromatic-Resins-Asphaltenes (SARA) and Gas Chromatograph (GC) data. The results indicate that the fluorescence spectra could be potentially used to estimate the chemical components of the crude oils. Saturates-Aromatic-Resins-Asphaltenes and Gas Chromatograph measurements are not available downhole, but fluorescence spectroscopy could be used to measure density stratification inside an oil reservoir, which can guide production strategies. It can alert production engineers to heavier crudes, which are less valuable and can be problematic to produce. It can also identify condensate-rich zones in wet gas reservoirs, so that these more valuable zones can be targeted for production.

Keywords: Optical sensors, CMOS sensors, Arduino, Fluorescence, Downhole tool, Oil density.

1. Introduction

The targeting of hydrocarbon reservoirs with favorable fluid properties is essential for increasing profitability for oil companies. As a result, the American Petroleum Institute (API) gravity (a measure of density) [1] is one important property that is measured to ensure that the fluids produced have economic value. Fluorescence measurements of oils can be used to estimate fluid properties, such as API gravity [2-4]. We have recently reported a miniaturized fluorescence measurement for small diameter logging tools [5]. In this work we discuss the dependence of the fluorescence spectra of crude oils on their chemical composition. Crude oil samples have to be carefully prepared in order to be representative of the reservoir fluids; therefore we propose a method of sample preparation to ensure sample uniformity. Further, we discuss how this fluorescence sensing platform can be used to target potential producing zones, both in conventional and unconventional reservoirs. In oil exploration and production a tool is typically deployed inside a well at the end of a conveying cable and chemical/physical properties of oils are measured by moving the tool from the bottom of the well. This is known in the oil industry as wireline logging [3].

2. Motivation

Accurately predicting the API gravity of oils in reservoirs is of great economic importance for oil production, both for conventional and unconventional prospects. Lighter oils and condensates (higher API gravity), for example, are frequently targeted by oil production companies. The cost of refining these hydrocarbon types is minimal compared to other heavier crudes. Condensates also provide valuable sources, such as ethane, for synthesizing plastics and other polymers. Thus, the profit per barrel realized makes producing lighter hydrocarbons more economically attractive and feasible. The economic value of lighter hydrocarbon fluids is also strongly related to the costs to produce them. This is especially true for unconventional reservoirs, where the small nanometer pore structures support relatively low permeabilities measured in nanodarcys [6]. In unconventional reservoirs, horizontal wells are drilled and then several hydraulic fracturing stages are used to increase the flow of the hydrocarbon fluids. Targeting optimal producing zones in parallel horizontal wells can be achieved by measuring properties of a producing well and using that information for the adjacent wells. This step has a critical economic impact, as it can reduce the length drilled and the number of hydraulic fracturing stages required for optimal hydrocarbon production. Unconventional oil reservoirs with nanometer pore sizes will have an increased production when lighter hydrocarbons are targeted. Fluorescence can be used to find such lighter fluids inside the borehole. Tracking the API gravity can be useful in determining if the oil produced matches the source maturity [7]. Anomalous API gravity trends are indications that the pressure inside the reservoir is decreasing too fast and only the lighter oils are being produced, leaving significant amounts of heavier oils behind. Targeting the optimum API gravity is also important in unconventional prospects. Lighter, more mature oil flows more easily in low permeability rocks than heavier oils, and these lower API gravity, more viscous oils are more challenging to produce economically. Measuring and predicting the API gravity for such reservoirs therefore helps to determine production costs and with facility planning. It has been shown that the fluid properties of produced oils can be measured and estimated using fluorescence spectroscopy. The API gravity is one property that shows a strong relationship to fluorescence [2]. Differences in fluorescence occur as the concentrations and types of polycyclic aromatic molecules change with maturity, which correlate to changing API gravity [3]. Therefore, developing a method using fluorescence to predict the API gravity and other fluid properties is essential to estimate the costs of producing different hydrocarbon types.

3. Geochemical Analysis Results

In this work, the 5 oil samples chosen for fluorescence measurements ranged from medium to condensate grades (API 28 to 46), and originated from conventional carbonate reservoirs. Biomarker analysis [7] of the oils correlate both with the API gravity and saturates, aromatics, resins and asphaltenes (SARA) fractions measured [8] (Table 1, Fig. 1) (Saturates-Sat, Aromatics-Aro, Resins, Asphaltenes-Asph). Fig. 1 plots typical Gas Chromatograph (GC) data in the C20 to C27 typical terpanes [7] biomarkers present in crude oils. These biomarkers are important in reservoir design for understanding the source of the oil and in refining processes where the type of output product (such as kerosene) needs to be maximized. Gas Chromatograph analysis is not available in situ and it requires injecting the oil sample into very long glass columns. Fluorescence spectra could be used to correlate the biomarker quantity to the biomarker content of the crude oils.

Table 1. API gravity and SARA percentage compositions of crude oils.

Oil	API	Sat	Aro	Resins	Asph
C-28	28.2	29.27	26.03	17.31	8.84
L-28	28.3	35.26	27.33	17.63	7.68
K-29	29.2	33.13	26.43	16.01	8.56
B-39	39.0	43.73	18.67	9.02	3.63
N-46	45.8	65.92	10.83	5.02	0.13

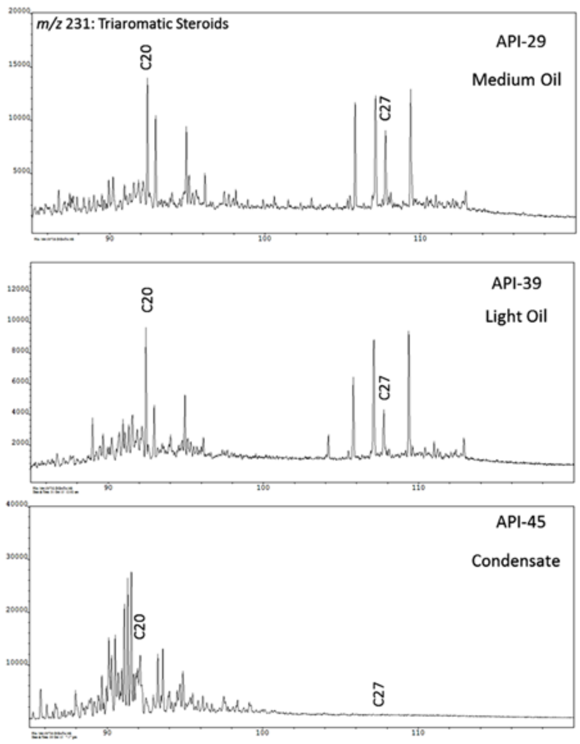

Fig. 1. Biomarker analysis showing changes in triaromatic steroids (C20 vs C27) for oils K-29, B-39 and N-46.

Maturity from biomarker measurements ranged from near peak oil to late oil to well into the condensate stage and were consistent with the increasing API's and the saturate/aromatic ratio (Fig. 1) [6]. API gravities measured are mainly related to the maturity of the oil source. We have to ensure that during the measurement the crude oil sample is not changing and it is representative of the oil samples encountered inside the borehole.

4. Benchtop Spectrometer Results

Fluorescence measurements were performed using a small optical spectrometer, model USB2000+, manufactured by Ocean Optics (Dunedin, FL) [9], a small 5 mW 405 nm laser, and a reflection probe. Before the oil samples were measured, they were thoroughly mixed using a vortex mixer. The homogeneity of the sample was checked with a small refractive index sensor manufactured by FISO Inc. (Ville de Québec, QC) and results are shown in Fig. 2. We used two sensors simultaneously, one near the top of the sample and one near the bottom. The RI values shown are the averages of the values given by the two sensors.

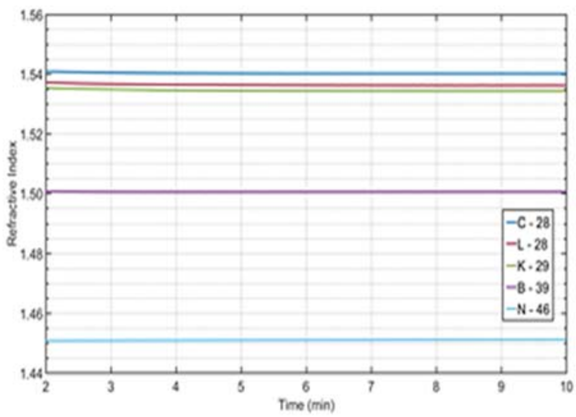

Fig. 2. Refractive index vs time for our oil samples.

As seen from Fig. 2 each sample has a stable refractive index over time, indicating that the heavier components in the oil are not segregating during our measurements. The refractive index correlates with the API gravity, with the heavier oils having larger refractive indices. This property can be used to distinguish oil from diesel-based drilling mud, since this type of drilling mud also exhibits fluorescence. Fluorescence measurements were performed on 10mL samples of each of the 5 oils, the results are shown in Fig. 3. Five milliliters of each sample were removed, had their fluoresence measured, and were then sent for a non-topping SARA analysis (Weatherford Laboratories method), in which traditional SARA is combined with GC to account for evaporation losses [8]. The SARA results are shown in Table 1. The remaining 5 mL of each oil sample had their fluorescence measured as well. For each of the oils there were three fluorescence measurements taken: the original 10 mL sample and the each of the two 5 mL samples after the original was split in half. All three measurements for three of the oil samples are shown in Fig. 4.

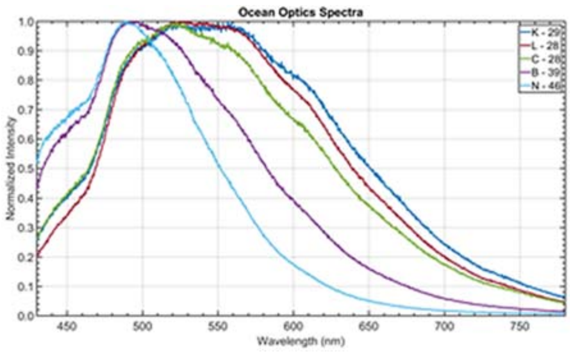

Fig. 3. Normalized fluorescence spectra of five oils using a 405 nm laser.

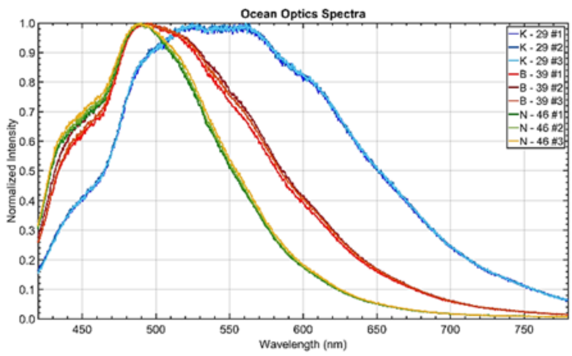

Fig. 4. Variability of optical fluorescence for three oil samples.

The results show that measurements were uniform and the variability between the three containers is small. The largest variability we see is with oil B-39. As the API gravity of the oil decreases, the fluorescence emission redshifts and broadens [2-3], which is consistent with the Urbach absorption. The redshift can be explained by considering that the lower API crudes have fused aromatic rings larger in size compared with those of the higher API gravity crudes [3]. The delocalized π electrons have a lower energy level when the fused rings are larger, resulting in emission at longer wavelengths.

5. Mini Spectrometer Optical Results

Our goal is to implement the fluorescence sensor in a small (43 mm diameter) wireline tool. The environmental requirements are 350 bar hydrostatic pressure and 100 °C operating temperature. For this purpose, we have used a small form Hamamatsu mini spectrometer model C12880MA-10 [10] (Bridgewater, NJ). The spectrometer has a 256 pixel CMOS sensor and a glass based diffraction grating. The spectrometer was integrated with an Arduino Nano microprocessor using a V3.0 Elegoo Nano board type CH340/Atmega328P. We performed a calibration measurement of both spectrometers using two known fluorescent dyes, Fluoro-Max Green and Red by Thermo Fisher Scientific. The response of both spectrometers was calibrated using a black body radiation source, Ocean Optics HL-2000-FHSA (Dunedin, FL). The results are shown in Fig. 5.

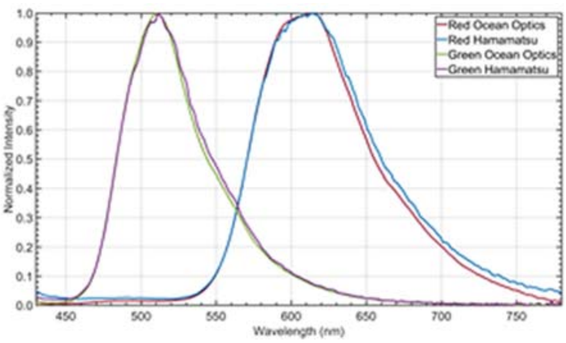

Fig. 5. Fluorescent dye spectra comparison.

The red/green fluorescence spectra match well after the instruments were calibrated. The calibration was done by taking into account the dark counts and the response of each instrument to a known black body radiation source. This calibration methodology needs to be used in any instance where two spectrometers are compared, as variability in responses can affect the results in some cases by as much as 25 %. Fig. 5 also indicates that although the CMOS sensor in the mini spectrometer has a factor of 10 fewer pixels than the Ocean Optics spectrometer, its spectral resolution is still sufficient for our measurement.

Fig. 6 presents an optical image of the mini spectrometer and the microcontroller.

Fig. 6. Optical image of mini spectrometer and Arduino microcontroller. USA Quarter for scale.

The small Hamamatsu board was used for ease of wiring. A diagram of the sensor circuit board is presented in Fig. 7. The actual Arduino code does not require the Hamamatsu board and the spectrometer is connected directly to the microcontroller which, in turn, is connected to a wireline main controller.

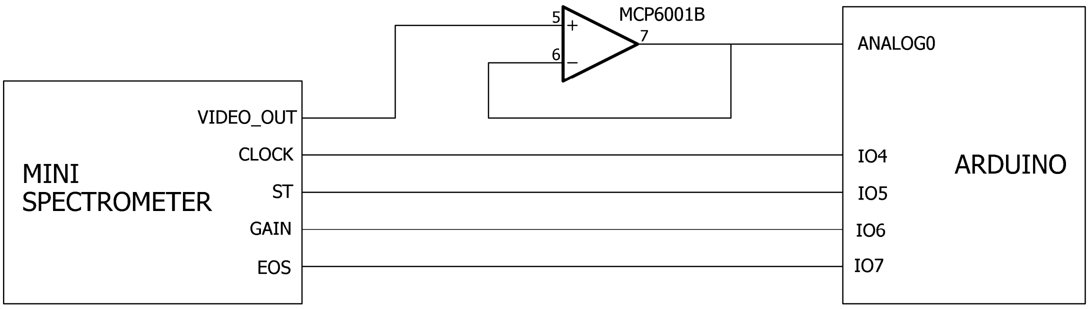

Fig. 7. Mini spectrometer electronic control diagram.

6. High Temperature Tool Implementation

The packages of the active optical components in our system are hermetically sealed to prevent damage due to moisture, i.e. the laser chip, the CMOS detector and the optical grating in the spectrometer. The hermetically sealed packages cannot be pressure compensated for the 350 bar required for our wireline logging tool. The TO56 laser and the C12880MA-10 mini spectrometer need to be housed inside the wireline tool at atmospheric pressure. Due to these requirements, we have opted for a fluorescence reflection probe which protrudes from the pressure housing of the tool. The pressure tolerant optical probe was manufactured by Custom Sensors Inc. (Fenton, MO). A picture of the wireline tool with two sensor ports is shown in Fig. 8. The housing for the electronics is shown on the left side of the top image. The tool can be connected to another logging module, via the connectors on the right side of the top image.

Fig. 8. Optical images of the fluorescence probe.

The bottom image of Fig. 8 shows the fluorescence probe inserted into the tool connector (left port). The optical probe has one 600 µm core fiber in the middle for the source and eighty-one 100 µm core fibers around the outside for the spectrometer arm. This geometry ensures a good signal for our samples. The tip of the probe is protected with a sapphire window suitable for harsh downhole conditions. The fluorescence probe uses one port, while the other port can be used for another type of fluid property sensor such as refractive index, density, viscosity, or temperature. A temperature probe is shown in the right port of the bottom image in Fig. 8.

Two models of miniature spectrometers were tested for dark voltage counts at elevated temperatures. The model C12666MA spectrometer has lower noise due to a lower gain, while the model C12880MA-10 spectrometer has higher sensitivity due to a higher gain. The results are plotted in Fig. 9 for the C12666MA spectrometer (top) and C12880MA-10 spectrometer (bottom). The dark counts increased with temperature due to increased leakage of the CMOS sensor and also due to high leakage in the amplifiers used after the CMOS sensor. The dynamic range of our CMOS sensor is ~5000 at 25 °C. The low limit is set by the dark counts in the pixel and the high limit is set by the 'depth' of the capacitor. As the temperature rises, the dark counts go up exponentially as seen in Fig. 9. At some temperature the dark counts will fill up the pixel completely and the CMOS sensor will be saturated. We can also consider the 5000 dynamic range of the sensor as a temperature dynamic range. With this temperature range (25-100 °C) we can measure more than 95 % of our targeted liquids wells. The C12880MA-10 spectrometer has ~150X more gain when compared with the C12666MA model. This sensitivity can be useful when measuring samples with lower fluorescence level such as heavier crude oils.

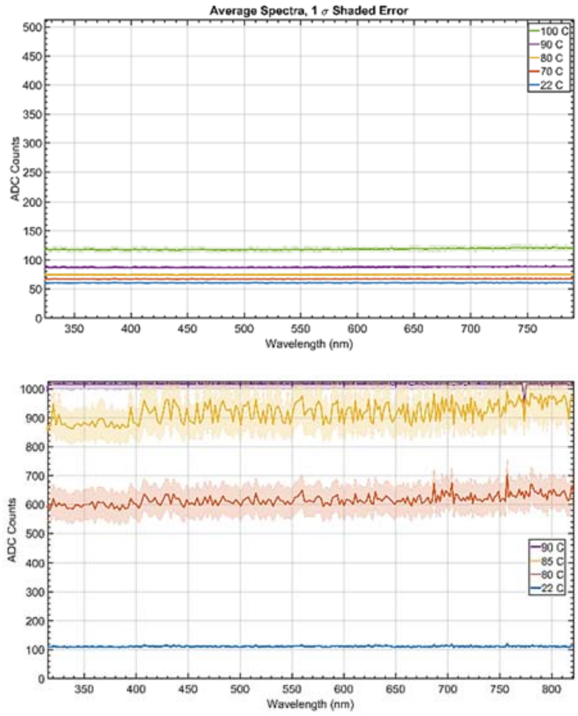

Fig. 9. Dark counts of the mini spectrometer at different temperatures for two models C12666MA (top) and C12880MA-10 (bottom).

7. Conclusions

In this paper we have investigated the relationship between chemical composition of hydrocarbon fluids (SARA) and optical fluorescence. We have shown that the density of an oil changes the shape of its fluorescence spectrum, with more mature sources (higher API gravity) having a blue shift compared to less mature oil sources (lower API gravity). We have also presented the integration of a mini spectrometer into a small diameter (43 mm) logging tool. The performance of the logging tool is similar to a benchtop, laboratory grade spectrometer. The optical measurement was integrated into the wireline tool using a high pressure (350 bar) fluorescence reflection probe. The probe itself is rated to a temperature of 150 °C. The miniature spectrometer was tested for high temperature operation. The results indicate that our logging tool could be used in most of the wells encountered in our application.

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