Sensors & Transducers, Vol. 239, Issue 12, December 2019, pp. 41-46

Sensors & Transducers

Published by IFSA Publishing, S. L., 2019
http://www.sensorsportal.com

Maturity Indicator Measurement using Novel Electron Paramagnetic Resonance Sensor

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Received: 4 November 2019 /Accepted: 4 December 2019 /Published: 9 December 2019

Abstract: Electron Paramagnetic Resonance (EPR) sensor systems can be used to measure free radicals and transitional metals in certain oxidation states, such as Mg^{2+} ,Mn^{2+},Co^{2+}, Cu^{2+}, Ni^{2+}, and Fe^{2+}. Organic free radicals are present in asphaltenes and in kerogen. Free radical concentration can be used as a maturity indicator for kerogen/oil. Traditionally, EPR sensors use a resonant electromagnetic cavity and a permanent magnet for measurements, which limits their size and makes them difficult to be miniaturized. In current EPR sensors the sample size is limited to several millimeters. In this work, we demonstrate an EPR sensor without the traditional transmission resonant cavity. An EPR measurement can be used as a maturity indicator for kerogen/oil, since it responds to free radicals present in organic matter. The advantage of the EPR sensor is that it can be designed to respond to kerogen material present in the source rock. Our EPR sensor is manufactured out of materials capable of withstanding borehole conditions. We intend to package this device in a small form factor such that it can be deployed into a 1 inch logging tool. Using such an EPR logging tool, we can identify sweet spots in horizontal wells and optimize the unconventional play. We will present data for several oil samples, as an example of oil maturity, and vanadyl porphyrin measurements. We will demonstrate that the EPR signal can be uniquely attributed to kerogen and can be easily correlated to a Hydrogen Index. The EPR imaging has a spatial resolution of 0.3 mm and can be used for heterogeneous samples such as source rocks. We will discuss the implementation of an EPR imaging system which could be used for core scanning/well logging. *Copyright © 2019 IFSA Publishing, S. L.*

Keywords: L Optical Sensors, CMOS Sensors, Arduino, Fluorescence, Downhole Tool, Oil Density.

1. Introduction

In exploration and production targeting hydrocarbon reservoirs with favorable fluid/gas properties is essential for increasing profitability for oil companies. Maturity and the density [1] of the hydrocarbon is essential in understanding the parameters of the reservoir for design and production optimization. There are several methods [2] to evaluate the maturity of the hydrocarbon/source and the most obvious one is Hydrogen Index (HI) which is related to the amount of H present in hydrocarbon [2, 4]. Traditional methods of measuring HI are time consuming and destructive-pyrolysis. HI can be derived from several types of measurements such as infrared spectroscopy, fluorescence and EPR [2]. In this work we report results for the use of EPR data for maturity prediction. We also discuss the implications of EPR data for the oil formation process. We present the design of a miniaturized ESR sensor for small diameter logging tools. This design is capable to be implemented in downhole conditions making the maturity prediction for exploration a much simpler task.

2. Motivation

Accurately predicting the maturity of hydrocarbon in reservoirs is of great economic importance for oil production both for conventional and unconventional prospects. Lighter oils and condensates for example, are frequently targeted by 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 the unconventional reservoirs where the small nanometer pore structure supports relatively low permeabilities measured in nanodarcys [3]. In unconventional reservoirs horizontal wells are drilled and then several hydraulic fracturing stages are used to increase the flow of the hydrocarbon liquids. Targeting optimal producing zones in parallel horizontal wells can be achieved by measuring a producing well and using that information for the adjacent horizontal wells. This step has critical economic impact as it can reduce the length drilled and the number of hydraulic fracturing stages required for optimal hydrocarbon production. Greater reservoir pressures and smaller hydrocarbon molecules, properties that are typical of condensate maturity for example, are optimal to recover hydrocarbons economically from these very tight formations. EPR measurements can be useful in determining if the oil produced matches the source maturity [4]. Anomalous maturity trends are indications that the pressure inside the reservoir is decreasing too fast and only the light oils are produced leaving significant amounts behind. Targeting the optimum oil maturity is also important in unconventional prospects. Lighter, more mature oil flows more easily in low permeability rocks than heavier oils, and these less mature, more viscous oils are more challenging to produce economically. Measuring or predicting the maturity for such reservoirs therefore helps to determine the costs to produce them. Fluid properties of produced oils have been shown to be measured and estimated using fluorescence spectroscopy. The ESR data shows a strong relationship to maturity [5]. Therefore, developing a predictive method using ESR to predict the maturity and other fluid properties is essential to mitigate the costs of producing different hydrocarbon types.

3. Geochemical Analysis Results

In this work, oil samples chosen for EPR measurements ranged from medium to light to condensate grades (API 28 to 46) and were originating from conventional carbonate reservoirs. Biomarker analysis [4] of the oils correlate both with maturity and saturates, aromatics, resins and asphaltenes (SARA) fractions measured [7] (Table 1, Fig. 1). (Saturares-Sat,Aromatics-Aro, Resins, Asphaltenes-Asph)

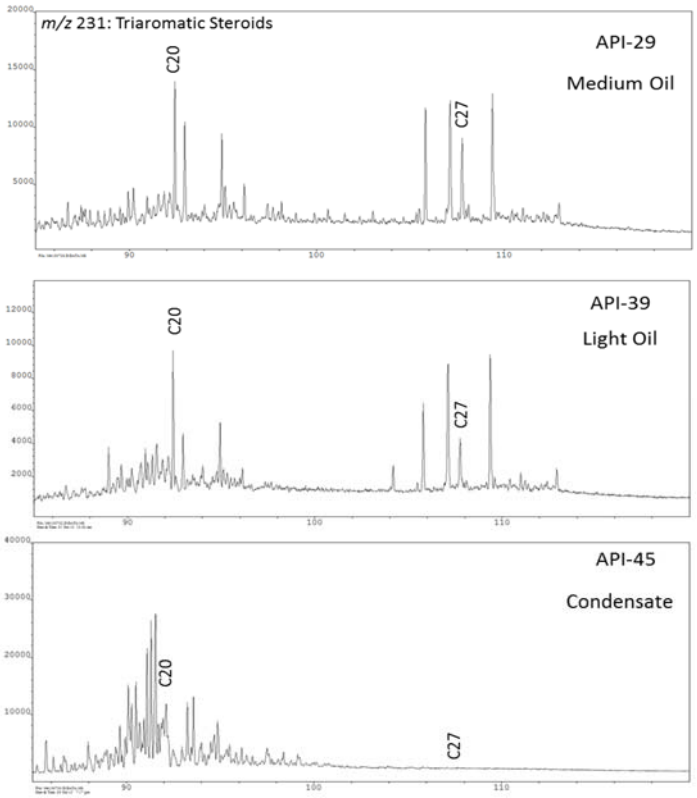

Fig. 1. Biomarker showing changes in triaromatic steroids (C20 vs C27) [10].

Maturity from biomarker measurements ranged from near peak oil to late oil to well into the condensate stage and were consistent with the increasing the saturate/aromatic ratio (Fig. 1) [6].

Table 1. API gravity and SARA percentage compositions of crude oils [10].

API	Sat	Aro	Resins	Asph
28.2	29.27	26.03	17.31	8.84
28.3	35.26	27.33	17.63	7.68
29.2	33.13	26.43	16.01	8.56
39.9	43.73	18.67	9.02	3.63
45.8	65.92	10.83	5.02	0.13

4. EPR Spectrometer Results

Electron Spin measurement is based on the interaction of the electron spin moment and an external field. This is known as a Zeeman Effect. The electron spin can have 2 values S=± ½. The difference between the energy of the two states is proportional to the intensity of an applied magnetic field B_0

$$\Delta E = g\,\mu_B B_0\,, \qquad (1)$$

where g is the gyromagnetic factor, μ_B is the Bohr magnetron. The energy difference between the two spin states can be varied by changing the intensity of the magnetic field B_0 (Fig. 2). When applying a fixed electromagnetic frequency and varying Bo an resonance will be created [9].

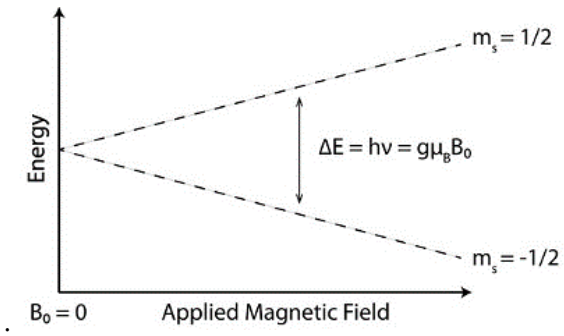

Fig. 2. Energy levels for an electron spin.

$$g = h\vartheta\,/\mu_B B_0 \qquad (2)$$

The gyromagnetic factor is an independent way of measure the molecular finger prints of different materials. Deviations of g from g=2 (value of the g for the electron in vacuum) contains the information about the molecule where the electron resides.

Elecron Spin measurements were performed using a small ESR spectrometer, model microESR, manufactured by Bruker [9]. Before the oil samples were measured they were mixed using a shaker. The homogeneity of the sample was checked with a small refractive index sensor manufactured by FISO Inc. (Ville de Québec, QC) [10]. ESR data was collected at room temperature and the results are plotted in Fig. 3.

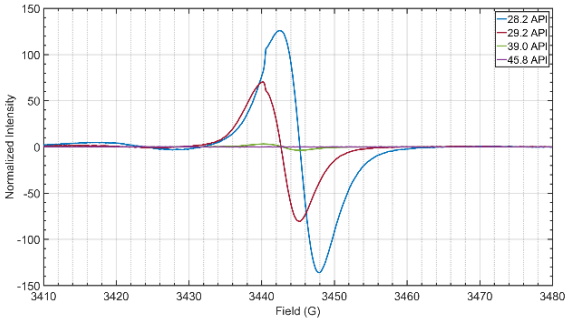

Fig. 3. EPR Spectra of the oils described in Table 1.

As seen from Fig. 3 the EPR signal has several important features. The large peak (3440G) is proportional to the free radicals concentration present in asphaltene [11] which is an indication of maturity. The condensate sample is more mature and the signal from this peak is greatly reduced.As the concentration of these radicals is reduced with increasing maturity this peak (3420G) can be used as a maturtity indicator. The second peak has a more subtle origin and it is caused by the VO^{2+}presennt in the asphaltenes [11]. This complex is part of the geoporphryn present in the oil samples [4]. Treibs [4] showed the link between the chlorophyl in living organisms and the porhyrins present in petroleum.The chlorophyls get converted during the diagenesis and catagenesis into deoxophyllo-erytroetio-porphyrins (DPEP) and etioporphyrins (etio),pristane and phytane [4]. During early diagenesis the Mg ion is removed and during the later diagenetic process the incorporation of metalls (V,Mn,Ga,Ni) occurs [4]. EPR signal correlate with SARA data presented in Table 1. The condensate sample has low asphaltene concentration and we can conclude that the ESR main peak is caused by the unpaired eletrons present in the fused aromatic rings[11].

Durand et al. [5] have used EPR to study kerogen with samples ranging from diagenesis to metagenesis. The signal first increases with temperature(maturity) then it decreases again. The initial increase is due to the elimination of the alkyl chains substituted on polyaromatic nuclei and it is related to oil and gas generation. The decrease of the signal as the maturity increases further it is lilkely caused be the breaking of larger molecues into smaller and smaller ones corresponding to the dry gas zones. Different types of kerogen will have different peaks due to the origin of the organic source, but within the same basin and with similar depositional enviroments the peak will not shift. This makes the EPR measurements useful for

tracking depositional conditions and type or maturation processes.We present in Fig. 4 EPR data for four kerogen samples with a HI ranging from 485 to 10. On the left axis we plot the iron and free radical concentration and on the right side axis we plot the HI.

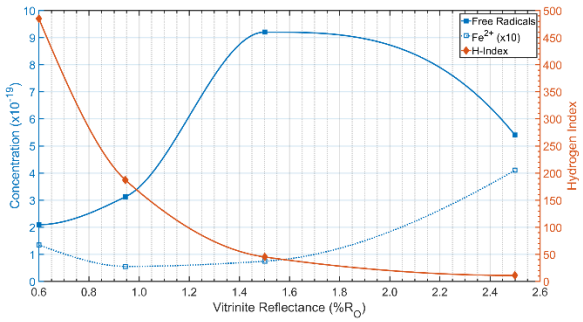

Fig. 4. EPR and HI data for kerogen samples vs $\%R_O$.

These kerogen samples also contain vitrinite used as a maturity indicator [2]. Vitrinite is a type of maceral present in the source rock and its reflectance in oil ($\%R_O$) is also used as a maturity indicator [2] In Fig. 4 on the left side of the plot we show the concentration of the free radicals present in the organic matter and the Fe^{2+} present in the pyrite which is also present in the source rock. There is a parabolic dependence of the EPR measurements similar with data reported previously [5] and the pyrite dependence is mirrored with the free radicals. The process of pyrite formation in sediments results from the action of bacteria, which reduces sulphate ions (dissolved in the pore water) to sulphide. If there is iron present, iron sulphide crystals begin to grow. These sulphate reducing bacteria also need other nutrients to live, which are provided by organic carbon in the sediment. As the organic matter matures there are more Fe^{2+} ions generated and when the maturation enters the later stages thre amount decreases [12]. There is a clear correlation between the EPR signal of the pyrite and the organic matter.

5. Mini Spectrometer ESR Design

Our goal is to implement the EPR sensor in a small 43 mm diameter wireline tool. The environmental requirements are 350 bar hydrostatic pressure and 100 Celsius operating temperature. Currently the smallest EPR device on the market is ~ 7cm and this particular device needs to be pressure compensated as it has a quartz electromagnetic cavity not capable of high pressure and temperature operation. A picture is shown in Fig. 5.

Aramco design, shown in Fig. 6, has 3 cm diameter and it uses a open resonator that is only several mm in diameter.On the right side of the device a plot of the DC magnetic field inside the sensing area in shown to demontrate the uniform reading. In the first prototype of the device the outer diameter of the ESR is 3 cm but in the future will be reduced to around 1.5-2 cm. The closed TEM cavity is sensitive temperature and it requires temperature control. In our commercial device there is a separate connector that monitors and controls the cavity temperature, and also the sample temperature. Fig. 7 shows a plot of the AC magnetic field inside the EPR device. The horizontal dimentions is ~ 2 mm and that would be our sensitive area. Uniformity of the magnetic field is shown to be good within the sampling zone ~6 A/m . The field plots are at the 2.97 GHZ frequency. Fig. 8 shows the simulation of the input reference AC voltage into the resonator and the reflected voltageat the output of the resonator, we have an estimated Q~100 in this case at 2.92 GHz.



Fig. 5. EPR module [9].

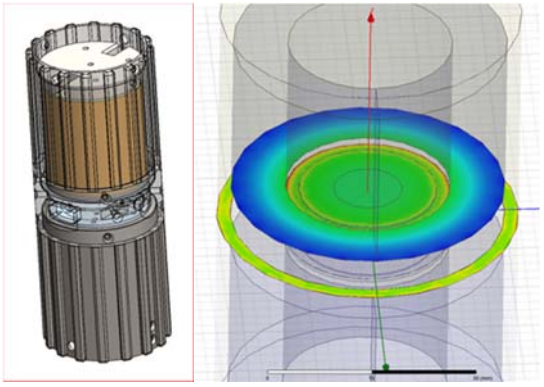

Fig. 6. Aramco EPR device and DC magnetic field.

We have also made 2D EPR images. In Fig. 9 results are shown for a transmission measurement at 9 GHz through a 3 mm thick sample. The goal was to examine that EPR techniques is suitable for 2D imaging. The color map represent the free radial concentration for a source rock sample ~ 6mm in diameter. The bedding layers can be seen as well as the areas with higher organic content show in red. This data demonstrates

that EPR could be used in 2D imaging and it will enable to build an insitu logging tool with borehole imaging capabilities.

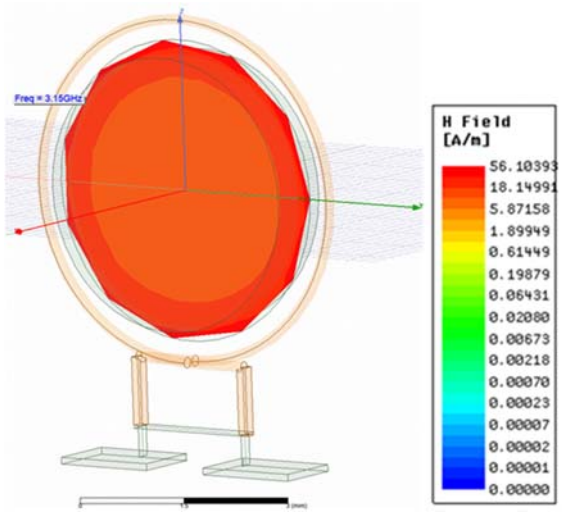

Fig. 7. Intensity of RF magnetic field inside EPR

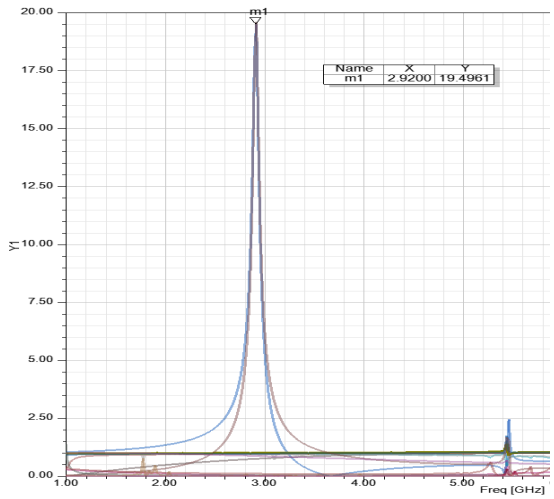

Fig. 8. EPR resonator Q design.

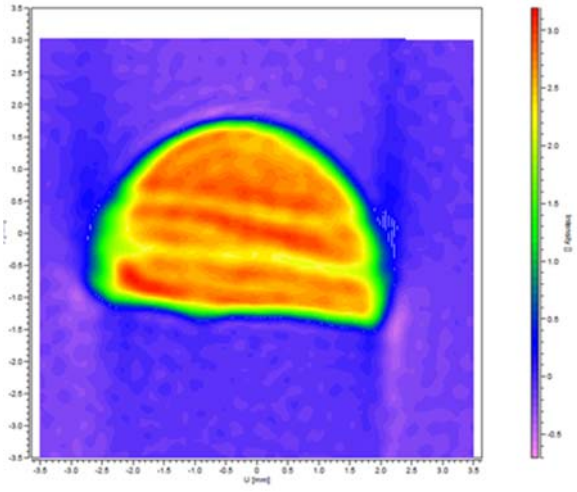

Fig. 9. 2D EPR image, field of view is 7×4 mm^2.

6. Conclusions

In this paper we have investigated the use of EPR hydrocarbon samples. The data presented indicated that EPR measurements can be used as a maturity indicator and can be correlated to geological indices such as hydrogen index. EPR spectrum has features that respond to changes in asphaltenes composition on oils. Geoporhyrins such as vanadyl porphyrin can also be measured. Data comparing EPR to geological maturity indicators, such as %RO and HI was presented. EPR measurements could be potentially used to infer sample maturity. We have shown a new EPR design which can be miniaturized to 20 mm diameter and does not require a TEM radio frequency cavity. This devices could be integrated into a logging tool with 43 mm diameter. We have shown that EPR imaging can be used to measure free radicals present in heterogeneous samples. A future design will implement an EPR imaging device which will be capable of creating borehole images to log maturity along the wells.

References

[1]. C. E. McGlade, A review of the uncertainties in estimates of global oil resources, *Energy*, Vol. 47, No. 1, Nov. 2012, pp. 262-270.

[2]. B. P. Tissot, and D. H. Welte, Petroleum formation and occurrence, *Springer Science & Business Media*, 2013, pp. 496-547, 237-244.

[3]. C. L. Cipolla, E. Lolon, and M. J. Mayerhofer, Reservoir modeling and production evaluation in shale-gas reservoirs, in *Proceedings of the International Petroleum Technology Conference*, 7-9 December, Doha, Qatar, January 2009.

[4]. K. E. Peters, C. C. Walters, and J. M. Moldowan, The biomarker guide, Vol. 1, *Cambridge University Press*, Cambridge, UK, 2005.

[5]. B. Durand, ed., Kerogen: Insoluble organic matter from sedimentary rocks, *Editions Technip*, 1980, pp. 243-270.

[6]. O. C. Mullins, The Physics of Reservoir Fluids: Discovery Through Downhole Fluid Analysis, *Schlumberger*, 2008.

[7]. Weatherford Geochemical Services https://www.weatherford.com/en/products-and-services/formation-evaluation/laboratory-services/geochemical-lab-analysis/

[8]. G. R. Eaton, S. S. Eaton, D. P. Barr, and R. T. Weber, Quantitative EPR, *Springer, Science & Business Media*, 2010.

[9]. Bruker https://www.bruker.com/products/mr/epr/microesr.html

[10]. S. Csutak, G. Bernero, and G. Ham, G., High Temperature Fluorescence Sensor for Oilfield Applications, *Sensors & Transducers*, Vol. 227, Issue 11, November 2018, pp. 82-87.

[11]. T. F. Yen, J. G. Erdman, A. J. and Saraceno, A. J., Investigation of the Nature of Free Radicals in Petroleum Asphaltenes and Related Substances by Electron Spin Resonance, *Analytical Chemistry*, 34, 6, 1962, pp. 694-700.

[12]. R. A. Berner, Sedimentary pyrite formation: an update, *Geochimica et Cosmochimica Acta*, 48, 4, 1984, pp. 605-615.

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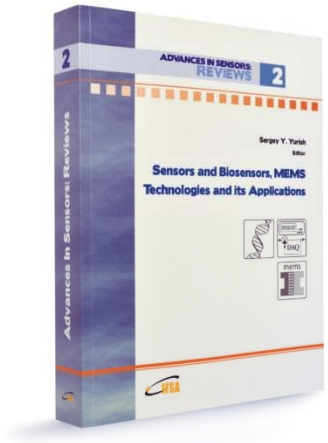

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