

Electronic Measurement of Vanadium and Asphaltenes by Micro-ESR

Asphaltenes can pose serious problems for crude oil producers and pipelines, by increasing viscosity of the crude and potentially fouling pipelines and equipment. At present, few technologies exist for on-line monitoring of asphaltene concentration in crude oil. Here we present a new advance in microwave sensor technology which enables continuous, on-line measurement of asphaltene and vanadium concentration in crude oil.

The underlying technology is Electron Spin Resonance (ESR), a field of magnetic resonance spectrometry that measures the concentration and composition of molecules with unpaired electrons.



Figure 1: Micro-ESR™ Oil Condition Sensor DIA.2.25”

ESR spectra of crude oil typically show a characteristic spectrum attributed to vanadyl porphyrins and asphaltenes. The exact chemical structure of asphaltenes is the subject of ongoing debate. However, it is generally accepted that asphaltenes produce an intense organic free radical ESR signal at $g=2.0032$ and vanadyl porphyrins produce an ESR spectrum with several broadly-spaced, narrow peaks (due to hyperfine splitting), a subset of which is measured by Micro-ESR.

Accurate measurement of the ESR spectrum of an unknown crude oil, along with simultaneous measurements of the microwave dielectric loss tangent and dielectric permittivity of the crude oil permits the Micro-ESR sensor to determine asphaltene concentration to within 0.05%, and vanadium concentrations as low as 5 ppm.

Background: Electron Spin Resonance

An electron spin resonance (ESR) spectrometer detects the concentration and composition of molecules with unpaired electrons present in a sample. The most common examples are free radicals and transition metal ions. The sample is loaded into a high frequency resonant cavity in a slowly varying uniform magnetic field. Unpaired electrons irradiated with microwave radiation at a fixed frequency will undergo resonant transitions between the spin 'up' and spin 'down' state at a characteristic magnetic field governed by equation 1, as shown conceptually in Figure 2:

$$h\nu = gBH \quad (1)$$

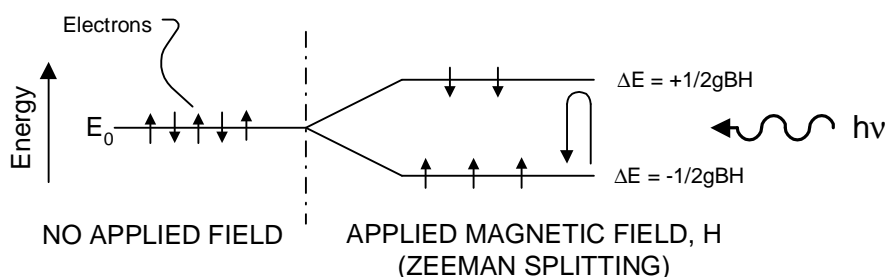


Figure 2: Electron transitions stimulated by incident microwave energy.

Here, h is Planck's constant, B is the Bohr Magneton, ν is the resonant frequency, H is the applied magnetic field, and g is a characteristic of the radical (the "g-factor," an empirically determined number, often close to 2.0032). The magnetic field at resonance is a function of the g-factor, and the height of the resonant peak is determined by the concentration of the radical in the sample.

Historically (since the ESR effect was first experimentally measured in 1945), ESR spectrometers have been designed using large water cooled electromagnets to generate a variable magnetic field. Conventional ESR spectrometers use a similar arrangement to that found in a nuclear magnetic resonance (NMR) spectrometer. This design has posed a significant hindrance in terms of portability, since the electromagnet assembly weighs upwards of 200 kg and requires several kW of power in operation. The Micro-ESR™ sensor has circumvented this problem by using a small, strong rare-earth magnet assembly with a low power 200 Gauss electromagnet coil. The sample is contained in a high-Q ceramic resonant cavity which has a large 'fill factor' relative to a conventional ESR. Thus sensitivity is improved but the size of the entire device is reduced by a factor of 1000.

Additional fundamental innovations in the design of the microwave bridge and receiver which now use modern low-cost components similar to those used in wireless communications devices have enabled dramatic cost reductions compared to conventional ESR spectrometers.

Experimental Results

We performed direct ESR measurements of five crude oil samples. The properties of the five crude oils are shown below. For comparison purposes, vanadium was measured by ICP and asphaltenes were measured by precipitation in n-heptane then weighed. The ESR scan takes about 45 seconds, compared to several hours for asphaltene precipitation.

Source	Vanadium (ppm)	Asphaltene (%)
Qua Iboe	2	0.2
Basrah Light	29	1.1
Vasconia	39	5.5
Meray	303	9.0
Oriente	65	12.0

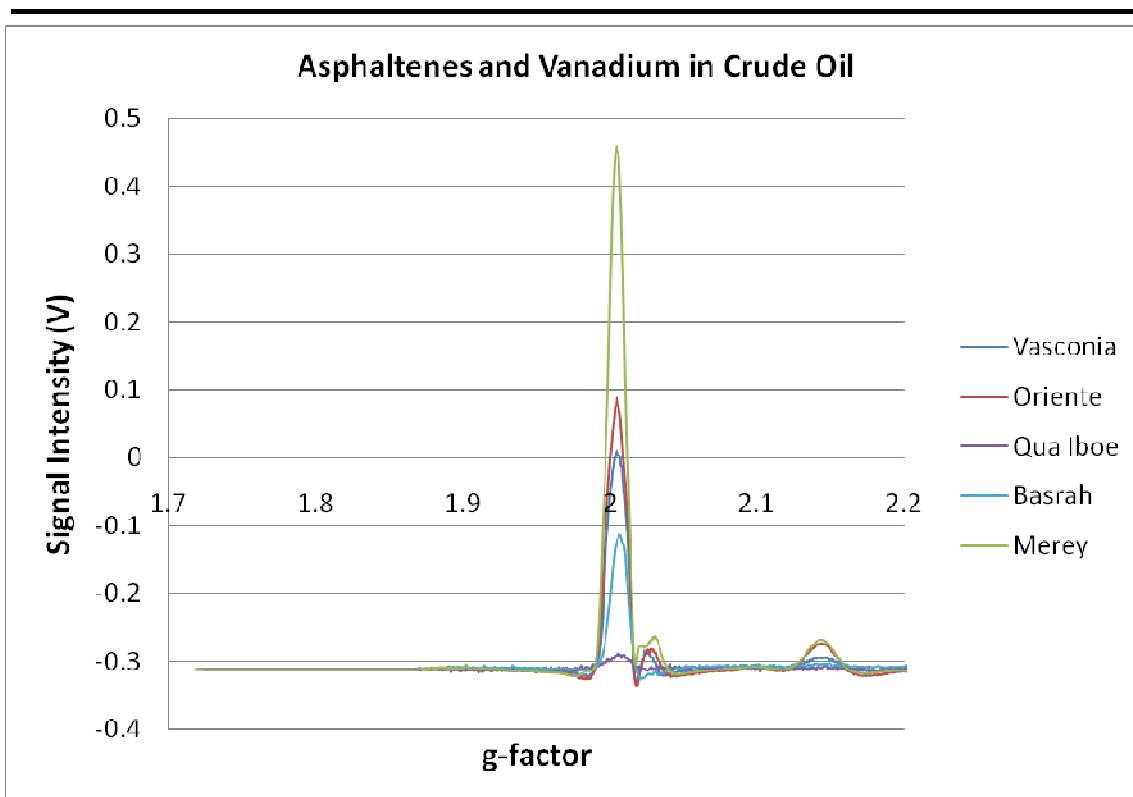


Figure 3: Asphaltenes and Vanadium in Crude Oil

As can be seen from the measured spectra shown in Figure 3, the area of the ESR peaks is not a simple linear function of the vanadium and asphaltene concentrations in the sample. Furthermore, the central peak is a combination of the vanadium and asphaltene signal while the peripheral peaks are vanadium alone. Curve fitting must be used to identify the contribution of each component to the central peak.

Another factor that must be considered is the variation in dielectric loss tangent between different oils. The Micro-ESR automatically measures the microwave power and cavity loaded 'Q', we can compute correction factors for each oil, tabulated below:

Source	Cavity Q	Microwave Power	Correction Factor
Basrah Light	293.5	-0.63 dB	1.106
Qua Iboe	312.8	-0.31 dB	1.000
Meroy	265.2	-1.56 dB	1.362
Vasconia	300.4	-0.71 dB	1.090
Oriente	302.6	-0.51 dB	1.058

From this, we can normalize the raw data relative to a reference oil. In this case we used Qua Iboe, which has almost no asphaltene or vanadium content. After normalizing the data, we can accurately compute the asphaltene and vanadium concentrations by analyzing the area under each curve. The correlations between ESR measured data and assay data are shown below.

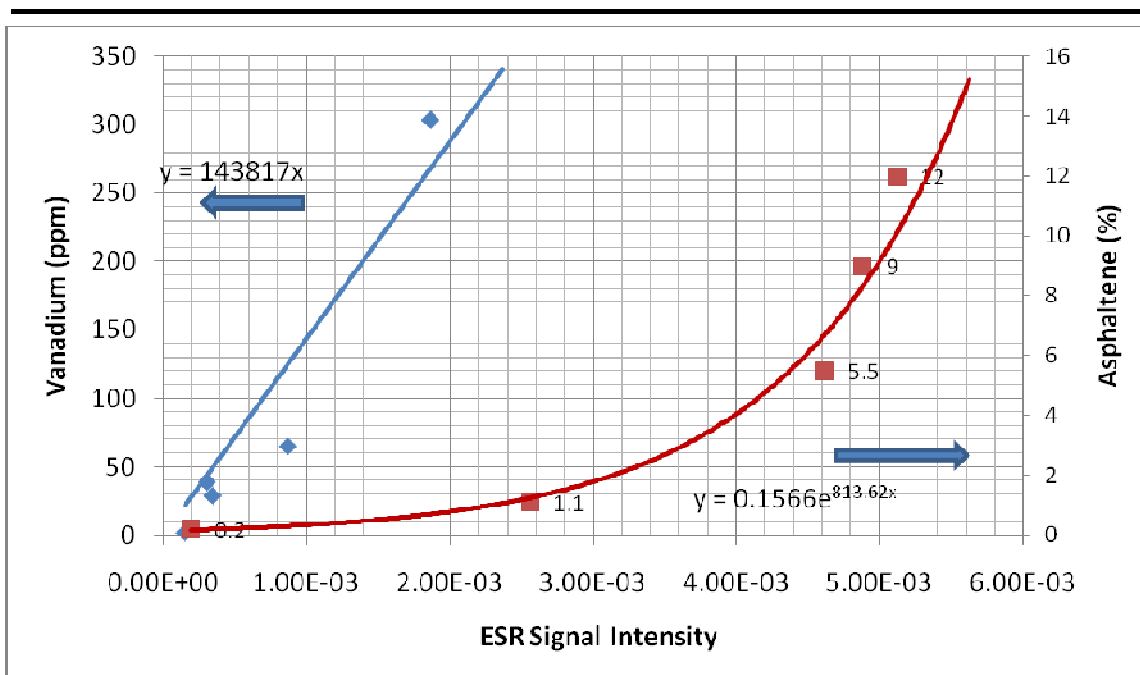


Figure 4: Vanadium and Asphaltene concentration vs. ESR Signal Area

As shown in Figure 4, vanadium concentration increases monotonically with the sum of the area under the $g=2.15$ and $g=2.02$ peaks. Asphaltene concentration grows exponentially with the area of the central peak, minus the contribution due to vanadium.

Conclusions

As has been known since the first commercial installation of an electron spin resonance spectrometer in an oil refinery, by Gulf Oil Co. in 1963, both vanadium and asphaltenes can be measured rapidly and precisely by ESR. However, new advances in low-cost, high frequency microwave electronics, combined with modern computer-aided design techniques have enabled us to build a highly miniaturized, rugged and relatively low cost instrument with very powerful on-line (or off-line) measurement capabilities. This development marks a fundamental shift in the cost-benefit equation for electron spin resonance spectrometry, opening up a wide range of applications in the petroleum industry, for example, monitoring asphaltene production in workover wells, asphaltene precipitation in pipeline operations, field assays of crude oil and oil-bearing sand and shale, and downstream applications in refining.