

## Measure vanadium, asphaltene concentration from the field

*Changes in asphaltene concentration over time can lead to increased fouling of machinery and pipelines and decreased production. A new sensor technology called Micro-ESR can rapidly and unambiguously detect the presence and concentration of asphaltenes in crude oil, online and onsite, where it counts.*

### AUTHORS

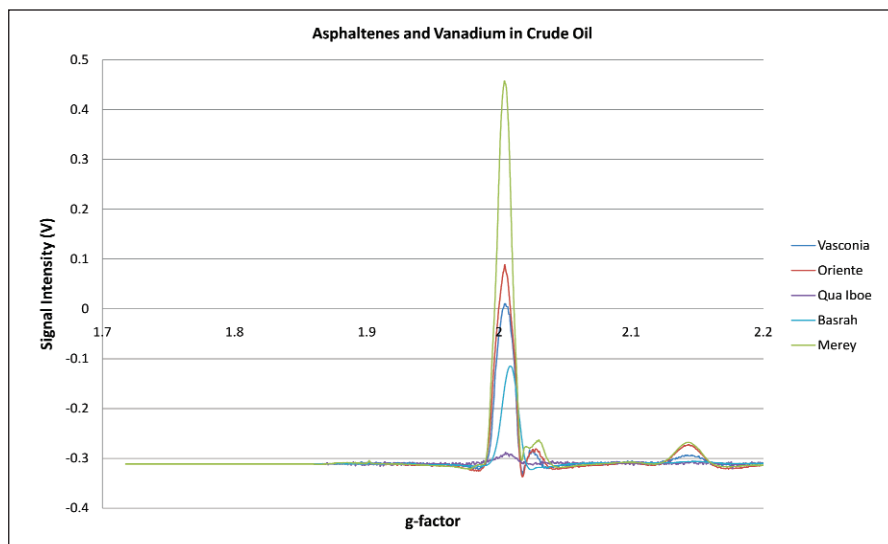
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Asphaltenes can pose serious problems for crude oil producers and pipelines by increasing viscosity of the crude and potentially fouling pipelines and production equipment. At present, few technologies exist for online monitoring of asphaltene concentration in crude oil. A new advance in microwave sensor technology now enables continuous, online 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.

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,



*Figure 1. The area of the ESR peaks is not a simple linear function of vanadium and asphaltene concentrations in the sample. 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. (Images courtesy of Active Spectrum Inc.)*

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. One of the key benefits of this technique is that it has extremely low sensitivity to so-called “cross-factors.” ESR is highly specific in the types of molecules in can detect.

### ESR

An 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 undergo resonant transitions between the spin “up” and spin “down” state at a characteristic magnetic field governed by the equation  $h\nu = gBH$ .

Here,  $h$  is Planck’s constant,  $B$  is the Bohr Magneton,  $\nu$  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 because the electromagnet assembly weighs upwards of 441 lb (200 kg) and requires several kilowatts of power in operation. Active Spectrum Inc.'s 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 1,000.

The microwave bridge and receiver now use modern low-cost components similar to those used in wireless communications devices. This has enabled dramatic cost reductions compared to conventional ESR spectrometers.

### Experimental results

Active Spectrum performed direct ESR measurements of five crude oil samples with a measurement time of approximately 45 seconds per sample. For comparison purposes, vanadium was measured by inductively coupled plasma, and asphaltenes were measured by precipitation in n-heptane, then weighed. It should be noted that the assay data for these samples was 10 to 15 years old therefore some variation between test results and the assay data could be expected.

Table 1. Direct ESR measurements of five crude oil samples.

SOURCE	VANADIUM (PPM)	ASPHALTENE (%)
Qua Iboe	2	0.2
Basrah Light	29	1.1
Vasconia	39	5.5
Merey	303	9.0
Oriente	65	12.0

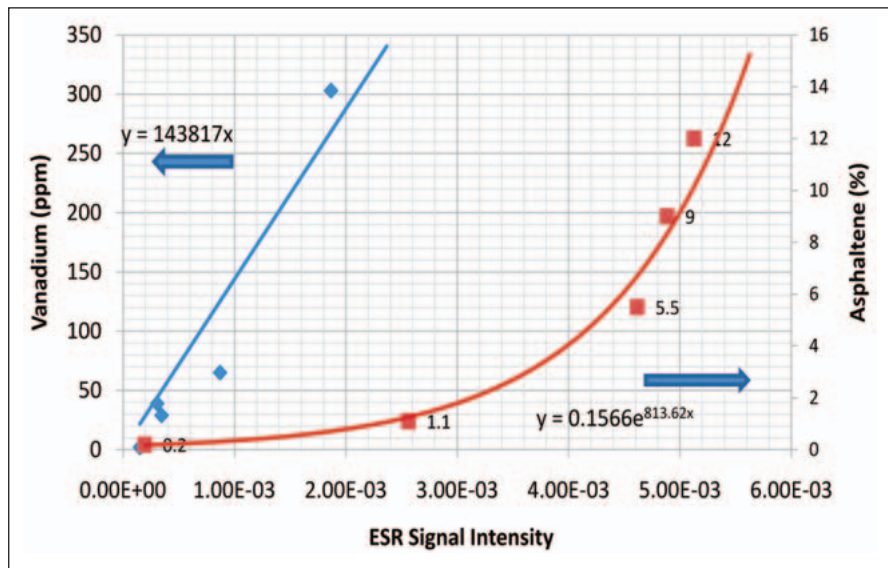


Figure 2. Micro-ESR can accurately compute asphaltene and vanadium concentrations by analyzing the area under each curve.

As can be seen from the measured spectra shown in Figure 1, 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 can 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. Micro-ESR automatically measures the microwave power and cavity loaded "Q." It is possible to compute correction factors for each type of oil.

From this, the raw data can be normalized relative to a reference oil. In this case Qua Iboe, which has almost no asphaltene or vanadium content was used. After normalizing the data, Micro-ESR 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 in Figure 2.

As shown in Figure 2, 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.

### Additional applications

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 Active Spectrum Inc. to build a highly miniaturized, rugged, and relatively low-cost instrument with very powerful online (or offline) 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. **ESR**