Micro Electron Spin Resonance: Unlocking Free Radicals

Free radicals are highly reactive chemical species that govern many fundamental chemical processes in nature, most notably combustion and oxidation. Until now, direct measurement of the composition and concentration of free radicals has represented a challenge for chemists due to the complexity and expense of the necessary equipment. A new innovation in sensor design, the Micro Electron Spin Resonance spectrometer (Micro-ESR™), offers the exciting potential of measuring free radicals with an extremely compact, low cost and ruggedized device.

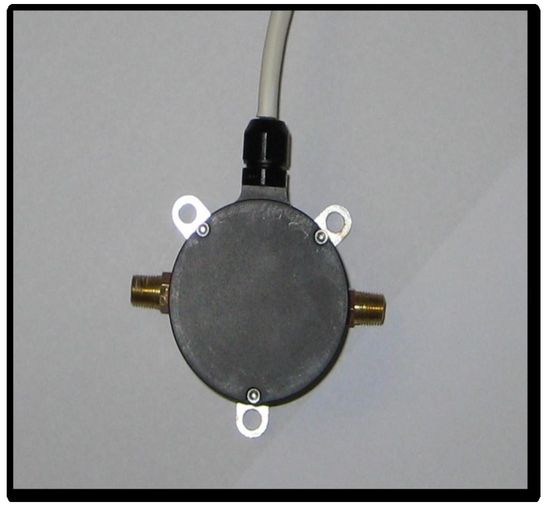

Figure 1: Micro-ESR™ Online Electron Spin Resonance Sensor Ø2.25".

Micro-ESR™ enables new low-cost applications such as on-line measurement of lubricant breakdown in engines and machinery, on-line airborne particulates monitoring in diesel engine exhaust and even spin immunoassay medical diagnostics.

Background: Electron Spin Resonance

An electron spin resonance (ESR) spectrometer detects the concentration and composition of free radicals present in a sample. Free radicals are atomic or molecular species with unpaired electrons which are usually highly reactive. 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:

$$h\nu = gBH \tag{1}$$

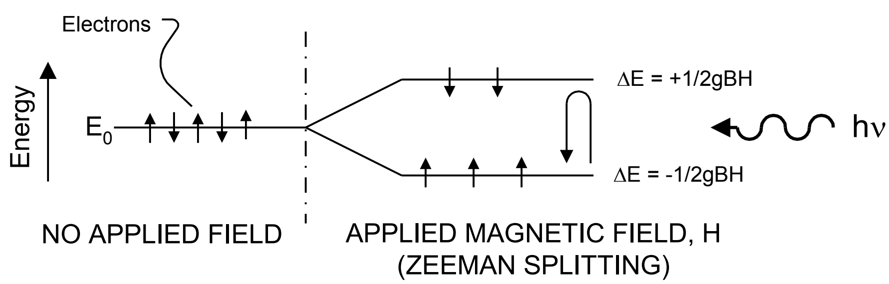

Figure 2: Electron transitions stimulated by incident microwave energy.

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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 2.0000). 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 further cost reductions by a factor of 1000 compared to conventional ESR spectrometers.

Experimental Results

Initial experiments to verify the operation of the Micro-ESR spectrometer were conducted with DPPH, a dye containing a stable free radical, dissolved in toluene solvent. DPPH dissolved in toluene exhibits a characteristic set of resonant peaks that correspond to hyperfine splitting.

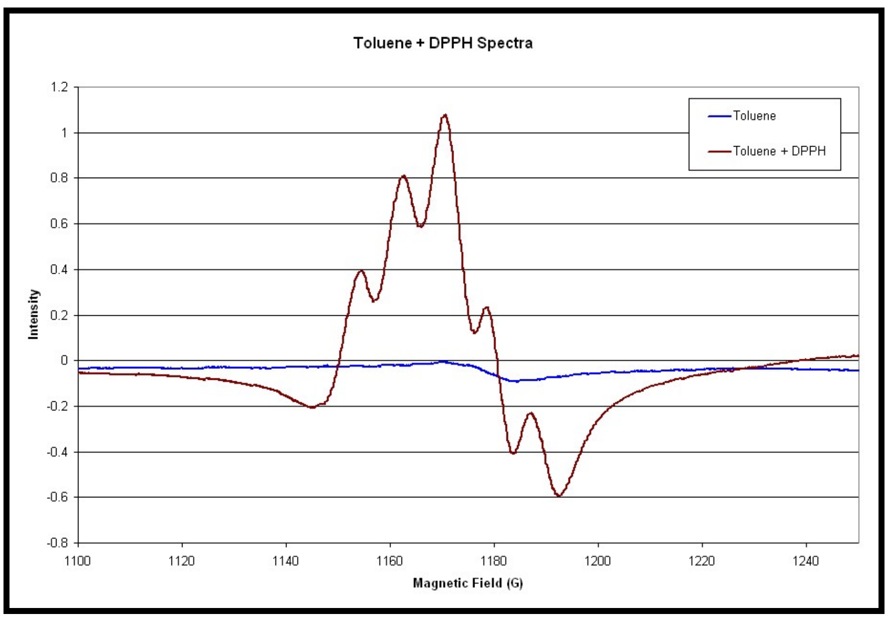

Figure 3: ESR Spectrum of 0.1% DPPH dissolved in Toluene showing hyperfine splitting.

A study of engine oil from a Honda gasoline engine was performed with ESR. As the antioxidant package in the oil is depleted by oxidation, the intensity of the peroxy radical ($RO_2\bullet$) signal increases steadily from zero. This is the induction period. Also, the g-factor of the peroxy radical signal increase slightly as the hydrocarbon chains are broken down. When the oil is approaching the end of its useful life, the intensity of the peroxy radical signal rises dramatically and failure is imminent as shown in Figure 4.

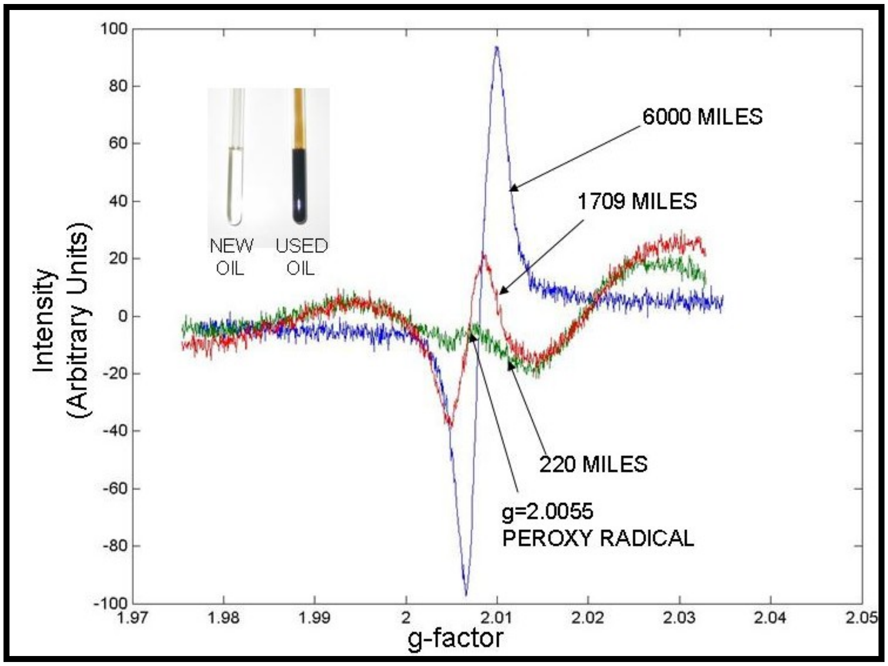

Figure 4: Peroxy radical vs. mileage (gasoline engine).

It is helpful to examine the oxidation chain reaction in more detail to understand the importance of the peroxy radical in lubricant breakdown. First, free radicals are produced by exposing oil to very high temperatures in the presence of oxygen (for example at the piston rings):

RH → R• (free radical) + H•
RH + O_2 → R• (free radical) + $HO_2\bullet$

The chain reaction then propagates as:

R• + O_2 → $RO_2\bullet$ (peroxy radical)
$RO_2\bullet$ + R'H → ROOH (hydroperoxide) + R'•

Normally, antioxidants are added to the base oil, which react with the peroxy radical and render it harmless. However, as the antioxidants in the oil are consumed, the concentration of peroxy radicals rises and breakdown accelerates.

A further study of marine engine cylinder lube oil from a 75,000-hp diesel engine was conducted to emphasize the flexibility of the Micro-ESR technique. Due to the poor quality bunker fuel typically burned in a large marine diesel, high levels of soot, and unburned fuel are commonly observed in the lube oil. In Figure 5, we clearly see both the soot and unburned fuel, which contains high levels of asphaltenes and vanadyl compounds. Cylinder lube oil is typically used once and then burned in the engine (a cargo ship uses approximately 1250 liters of lube oil per day which represents a substantial operating expense). Lube oil feed rates can however be reduced by ship operators who seek to minimize operating costs, as long as unburned fuel contamination limits are not exceeded.

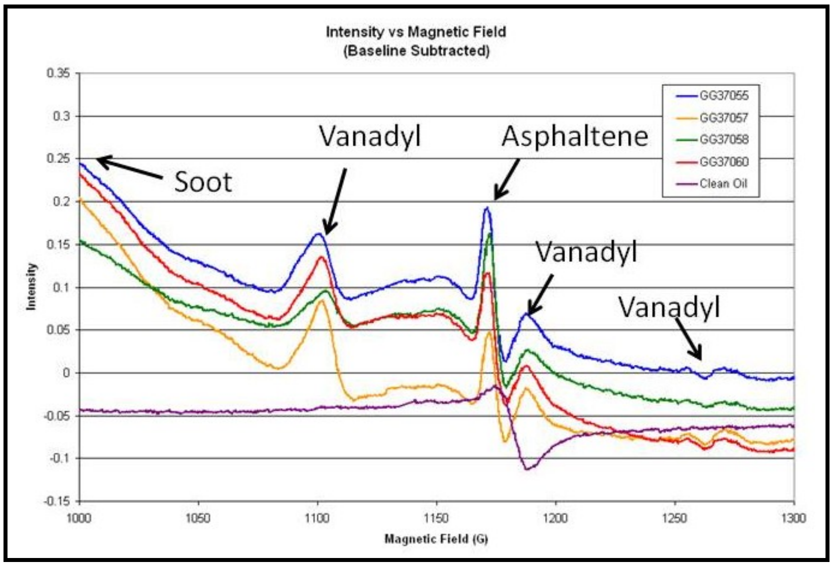

Figure 5: ESR spectra of marine engine lube oil samples.

Applications

In terms of on-line lubricating oil analysis, the above examples clearly indicate the breadth of applications (100 hp gas motors to 75,000 hp marine diesels) where the sensor can be applied. Operators of all types of industrial diesel engines are continually seeking out new ways to reduce operating costs and eliminate equipment downtime (or in the case of military users, improve operational reliability). Extended oil drain intervals reduce downtime and maintenance costs, which can be substantial in the case of remotely situated equipment such as oilfield artificial lift pumps or large diesel generators in continuous operation in the field. Furthermore, routine oil analysis programs are wasteful since the vast majority of manually obtained oil samples (92% in the case of the Army Joint Oil Analysis Program) are determined to require no action from maintenance staff. Sophisticated, embedded oil analysis sensors such as Micro-ESR can reduce routine oil analysis overhead and related downtime by a factor of 10, while providing instant notification of lubricant failure conditions.

As shown in Figure 5, carbon soot particulates can readily be detected by Micro-ESR, both when dissolved in the oil, and also from airborne soot. This offers the possibility of using Micro-ESR to measure both composition and concentration of airborne soot particulates in vehicle or powerplant emissions. Just as an oxygen sensor in a gasoline engine is used to adjust the fuel-air mixture to prevent the engine from running too rich, a Micro-ESR airborne soot sensor could be used to adjust the fuel-air mixture in a diesel engine to prevent excess particulate emissions. This is an increasingly important application as new emissions standards are continually challenging vehicle manufacturers to reduce particulate emissions.

Competitive Advantages

The primary competitive advantage of Micro-ESR over all other on-line oil analysis techniques is that Micro-ESR measures intrinsic chemical properties of the oil (concentration of chemical constituents) while all other approaches measure physical properties of the oil (dielectric constant, viscosity, electrical impedance, etc.) and then try and relate that data to underlying chemical changes in the oil. The "physical property" approach fails in practice since no laboratory-derived model of oil degradation can properly account for the breadth of operating conditions found in the field. The presence of multiple factors can easily confound less sophisticated measurement techniques (e.g. simultaneous fuel and water contamination of the oil), and no amount of data processing, computer modeling or artificial intelligence can compensate for fundamentally flawed sensor data.

A further advantage is that Micro-ESR gives an "absolute" reading of the condition of the oil. New oil has a "null" spectrum—there are no free radicals, carbon or other contaminants present in the oil. The presence of any ESR spectrum indicates unambiguously that contamination is present in the oil.

In addition, the "g-factor" (see equation 1) of each free radical is only very weakly dependent on temperature. Since free radicals in oil can be uniquely identified by their "g-factors," this allows the user to easily identify any ESR signals with absolute confidence at any operating temperature. The specificity of ESR means that no compounds other than free radicals or transition metal ions will produce a signal. The technique therefore does not exhibit cross-factors commonly seen with other sensors.

Since the dielectric constant of the oil is measured directly (and very accurately) by this sensor, along with the insertion loss of the microwave cavity, the user can obtain precise information about the concentration of water (or other polar liquids) in the sample. This information is most commonly of interest in applications where moisture intrusion can severely compromise gear and bearing life.

Last, in the case of airborne soot particulates, there is currently no low-cost sensor available on the market that can detect both composition and concentration of carbon soot. This application of Micro-ESR offers the end-user a new and low cost way to ensure compliance with environmental standards. It also permits the user to identify when an engine is running too rich (due to a clogged air filter or malfunctioning injector pump, for example) which severely reduces fuel efficiency.

Summary

Micro-ESR represents a fundamental advance in the state of the art of chemical sensor technology. Despite the enormous breadth of applications of electron spin resonance spectrometry (over 23,500 citations in PubMed for example), there have been no fundamental advances in the core design of the spectrometer until now. Micro-ESR is poised to revolutionize free radical chemistry by bringing unprecedented analytical power to the mainstream user.

Typical Uses

The Active Spectrum Micro-ESR™ Oil Condition Sensor is targeted for use in vehicle fleets including military vehicles, heavy trucking, shipping, rail, heavy equipment, power generation and wind turbines. Any industrial machinery with stringent lubrication requirements could benefit from accurate, on-line condition-based maintenance.

Availability

The Micro-ESR™ Lubricant Condition Sensor is currently available for purchase in pre-production quantities for evaluation purposes. Interested parties please contact Dr. James White at +1 650-610-0720 or jwhite@activespectrum.com.

Technical Specifications

The Active Spectrum Micro-ESR™ Lubricant Condition Sensor uses a microwave resonance signal to measure the concentration of free radicals in lubricating oil.

Supply Voltage	**12-32 VDC, 2.0A**
Sensor Output Options	**USB, Modbus®. Additional communication standards are available according to customer specifications.**
Dimensions:	**2.25” ϕ x 1.5” tall cylindrical metal package with hydraulic and electrical connections.**
Fittings	**1/8” NPT.**
Quantities Measured	**Oxidation, Soot (Peroxy Radical and Carbon Radical), Water Content, fuel dilution (marine bunker fuel only), RF dielectric permittivity.**
Operating Temperature Range	**-30°C to +85°C**
Max. Inlet Oil Temperature	**160°C+**