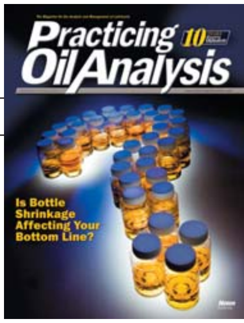

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INSTRUMENT REVIEW

Unlocking Free Radicals with Micro Electron Spin Resonance

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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.

An innovation in sensor design, the Micro Electron Spin Resonance spectrometer (Micro-ESR), measures free radicals with a compact, low-cost and ruggedized device.

The spectrometer enables new low-cost applications such as online measurement of lubricant breakdown in engines and machinery, online 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, shown conceptually in Figure 2.

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.

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 more than 200 kilograms (kg) and requires several kilowatts (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

Figure 1. Micro-ESR Sensor

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.

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 further reduced costs by a factor of 1,000 compared to conventional ESR spectrometers.

Experimental Results

Initial experiments to verify the operation of the 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.

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 increases 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 increases dramatically and failure is imminent, as shown in Figure 3.

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 high temperatures in the presence of oxygen (for example at the piston rings):

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

The chain reaction then propagates as:

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

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 increases and breakdown accelerates.

A further study of marine engine cylinder lube oil from a 75,000-horsepower diesel engine was conducted to emphasize the flexibility of the electron spin resonance technique. Due to the poor-quality bunker fuel typically burned in a large marine diesel, high levels of soot, sulfur compounds, dissolved metals and oxidation are commonly observed in the lube oil. In Figure 4, all of these compounds can be observed experimentally.

Cylinder lube oil is typically used once and then burned in the engine (a cargo ship uses approximately 1,250 liters of lube oil per day, which represents a substantial operating expense). Lube oil feed rates must also be adjusted depending on the concentration of sulfur in the fuel oil, and measurement of the sulphur content of the fuel is of interest to ship operators who seek to minimize operating costs.

Applications

In terms of online 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 continually seek new ways to reduce operating costs and eliminate equipment downtime

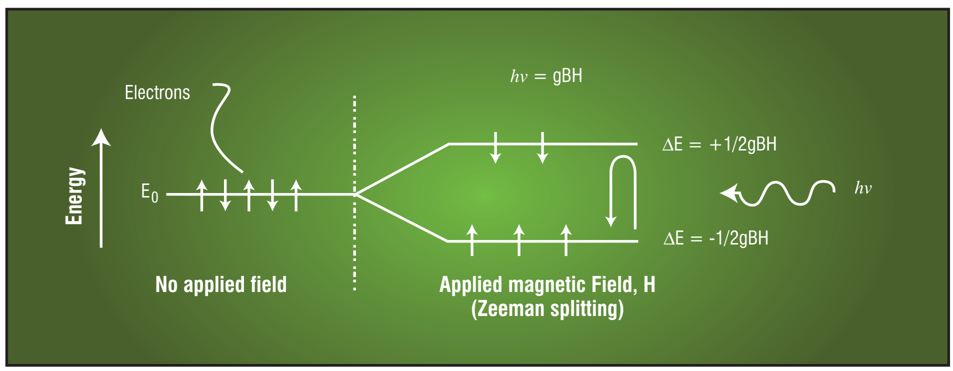

Figure 2. Electron Transitions Stimulated by Incident Microwave Energy

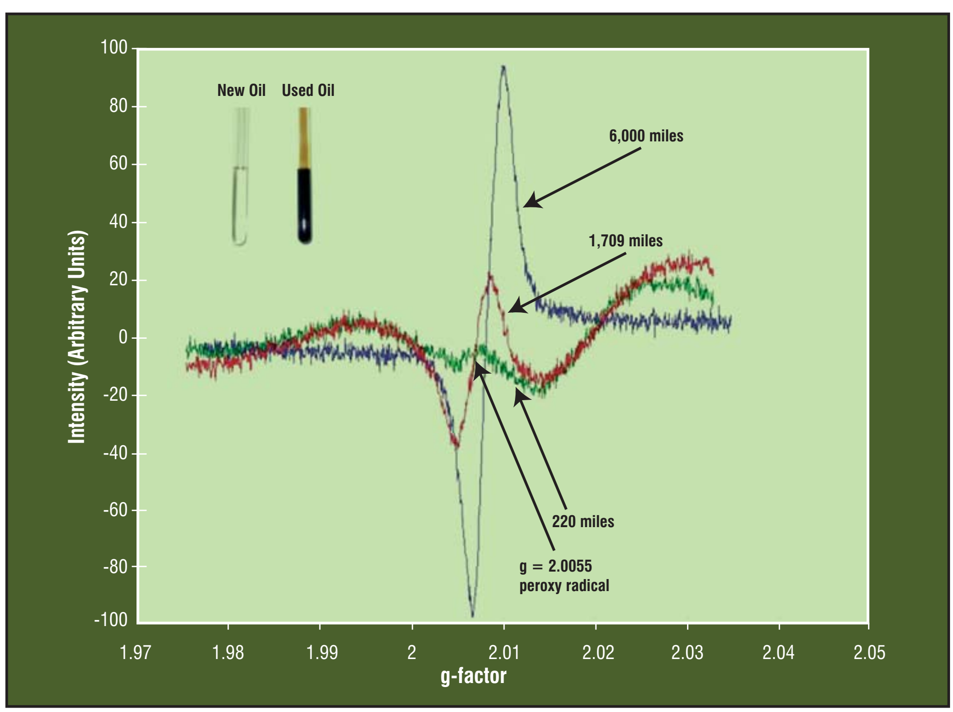

Figure 3. Peroxy Radical vs. Mileage (Gasoline Engine)

(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 because the vast majority of manually obtained oil samples (92 percent 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 this spectrometer 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 4, carbon soot particulates can readily be detected by the spectrometer, both when dissolved in the oil and also from airborne soot. This offers the possibility of using it 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, an electro spin resonance 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.

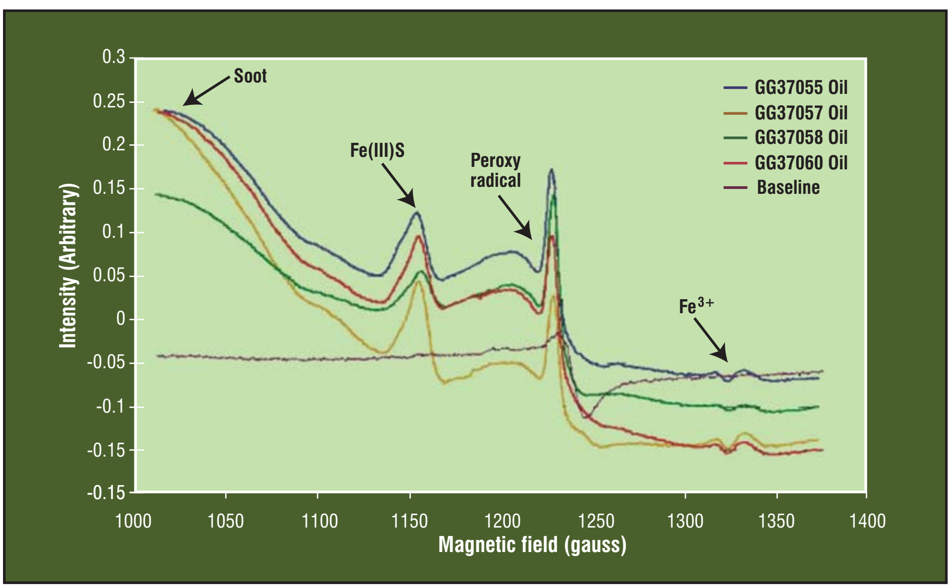

Figure 4. ESR Spectra of Marine Engine Cylinder Lube Oil Samples

Supply Voltage	12-32 VDC
Sensor Output Options	USB, Modbus®, RS-232, Ethernet, CAN. Additional communication standards are available according to customer specifications.
Dimensions:	2.25-inch ϕ by 1.5-inch tall cylindrical metal package with hydraulic and electrical connections.
Fittings	7/16-inch JIC, NPT, others available according to customer specifications.
Quantities Measured	Oxidation and soot (peroxy radical and carbon radical), water content, fuel dilution (marine applications only), RF dielectric permittivity.
Operating Temperature Range	-30°C to +120°C
Max. Inlet Oil Temperature	160°C+

Table 1. Specifications

Competitive Advantages

This spectrometer measures intrinsic chemical properties of the oil (concentration of chemical constituents), while other approaches measure physical properties of the oil (such as dielectric constant, viscosity, electrical impedance) and then relate that data to underlying chemical changes in the oil.

The physical-property approach fails in practice because 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 (for example, 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.

Another advantage is that the spectrometer 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 clearly indicates that contamination is present in the oil.

In addition, the g-factor (see Equation 1) of each free radical is only weakly dependent on temperature. Because 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.

Because the dielectric constant of the oil is measured directly and 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.

Lastly, 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 the spectrometer 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 (more than 23,500 citations in PubMed, for example), there have been no fundamental advances in the core design of the spectrometer until now. This spectrometer is poised to revolutionize free radical chemistry by bringing unprecedented analytical power to the mainstream user.

Typical Uses

The spectrometer 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, online condition-based maintenance.

Technical Specifications

The spectrometer uses a microwave resonance signal to measure the concentration of free radicals in lubricating oil. **POA**

Acknowledgment

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About the Authors

In his role as the chief technical officer of Active Spectrum Corporation, Chris White is responsible for microwave design and electronics integration.

James White is president and co-founder of Active Spectrum, in charge of all aspects of mechanical design and development of sensors, tunable filters, oscillators, packaging and control systems.

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About the Company

Information about the company can be found at www.activespectrum.com.