

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 easily measuring free radicals with an extremely compact, low cost and ruggedized device.

Active Spectrum's Micro-ESR™ enables new applications such as on-line measurement of lubricant breakdown in hydraulic systems, gas turbines, engines and machinery, raw fuel dilution in marine engine lubricants, thermal coking of gearbox oils. Many other applications in the petrochemicals industry exist including measurement of asphaltene and vanadium content in crude oils, petrochemical additives and related applications.

In this paper, we summarize the test data and results we have obtained using this new technology to analyze a wide range of lubricants and crude oils. The quick-reference below will help direct you to the relevant data for each subject:

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Figure 1: Micro-ESR™ Online Oil Analysis System, 10" x 8" x 5".

Please contact us directly at sales@activespectrum.com or +1 650-212-2625 to discuss your application in more detail. We can also accept a small number of test samples for a free demonstration of the technology.

Background: Electron Spin Resonance Spectroscopy

An electron spin resonance (ESR) spectrometer detects the concentration and composition of free radicals present in a sample. The sample can be a liquid, solid or gas. 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:

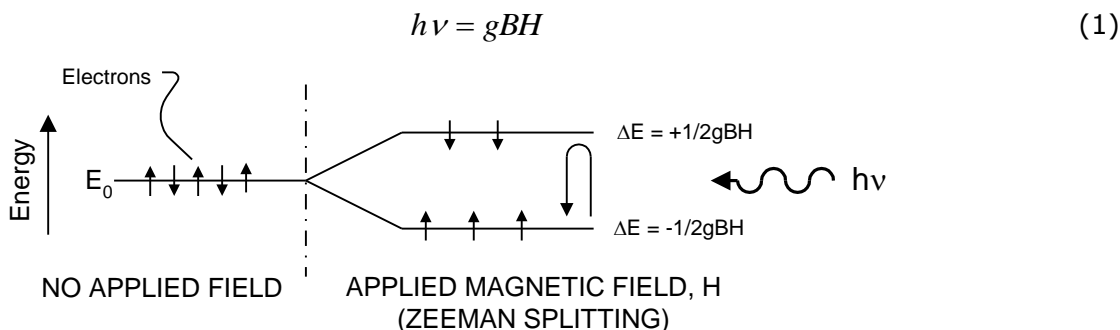


Figure 2: Electron transitions stimulated by incident microwave energy.

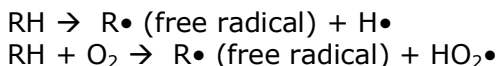
Here, h is Planck's constant, B is the Bohr Magneton, ν is the resonant frequency, H is the applied magnetic field, and g is a characteristic of the radical (the "g-factor," an empirically determined number, often close to 2.0000). The magnetic field at resonance is a function of the g-factor, and the double integral 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 older nuclear magnetic resonance (NMR) spectrometers. 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. Our Micro-ESR™ spectrometers have circumvented this problem by using a small, strong rare-earth magnet assembly with a low power electromagnet coil. The sample is contained in a high-Q resonant cavity which has a large 'fill factor' relative to a conventional ESR. Thus high sensitivity can be obtained but the size of the entire device is reduced by a factor of 100.

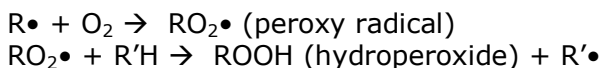
Additional fundamental innovations in the design of the microwave bridge and receiver, which now use modern low-cost integrated components similar to those used in wireless communications devices offer further cost and size reductions compared to conventional ESR spectrometers. Our innovations have resulted in a fundamental shift in the field of ESR spectroscopy, away from large centralized spectroscopy systems towards small, distributed sensing in real time, in the field, where it matters.

Application to Lubricant Degradation

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

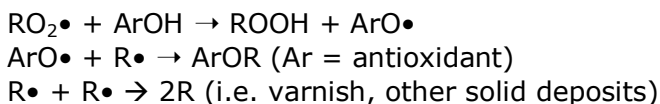


The chain reaction then propagates as:



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.

Some typical termination reactions are as follows:



The stable free-radical species produced as a result of oxidation reactions are what gives rise to the ESR signals measured by the Micro-ESR spectrometer. As will be shown below, these oxidation signals correlate well with other ASTM-standard measurements, in particular, FTIR spectroscopy.

Instrument Specifications

Active Spectrum's Micro-ESR™ Oil Analysis System uses a miniature electron spin resonance spectrometer measure the concentration of free radicals in liquids. The spectrometer operates at a frequency of 9.5 GHz with a highly uniform, miniature magnet centered at 3480 Gauss +/- 150 Gauss.

Specification	Value
Supply Voltage	15 VDC, 6.7A
Sensor Output Options	USB. Additional communication standards are available according to customer specifications.
Dimensions:	Approx. 9" x 12" x 5" stainless steel enclosure. See outline drawing for exact dimensions.
Operating Temperature Range	-30°C to +55°C / 90% RH

Fluid System

Internal Flow Cell	6mm OD x 4mm ID Reinforced Teflon Tube
Fittings	1/4" Swagelok or 6mm Parker stainless steel tube fittings
Max. Inlet Oil Temperature	160 °C
Max. Inlet Oil Pressure	150 psi

RF System

RF Signal Source	VCO (-119 dBc/Hz @ 100 kHz offset from carrier) OR YIG Oscillator (-132 dBc/Hz @ 100 kHz offset)
RF Power Level	1 mW to 80 mW, controllable by 4-bit digital attenuator
Cavity Unloaded Q (Q _u)	2500 +/- 10%
Receiver architecture	2-channel carrier-suppressed homodyne receiver
Phase Control	6-bit Digital Phase Shifter
Cavity Coupling Adjustment	Servomotor-tuned iris coupler

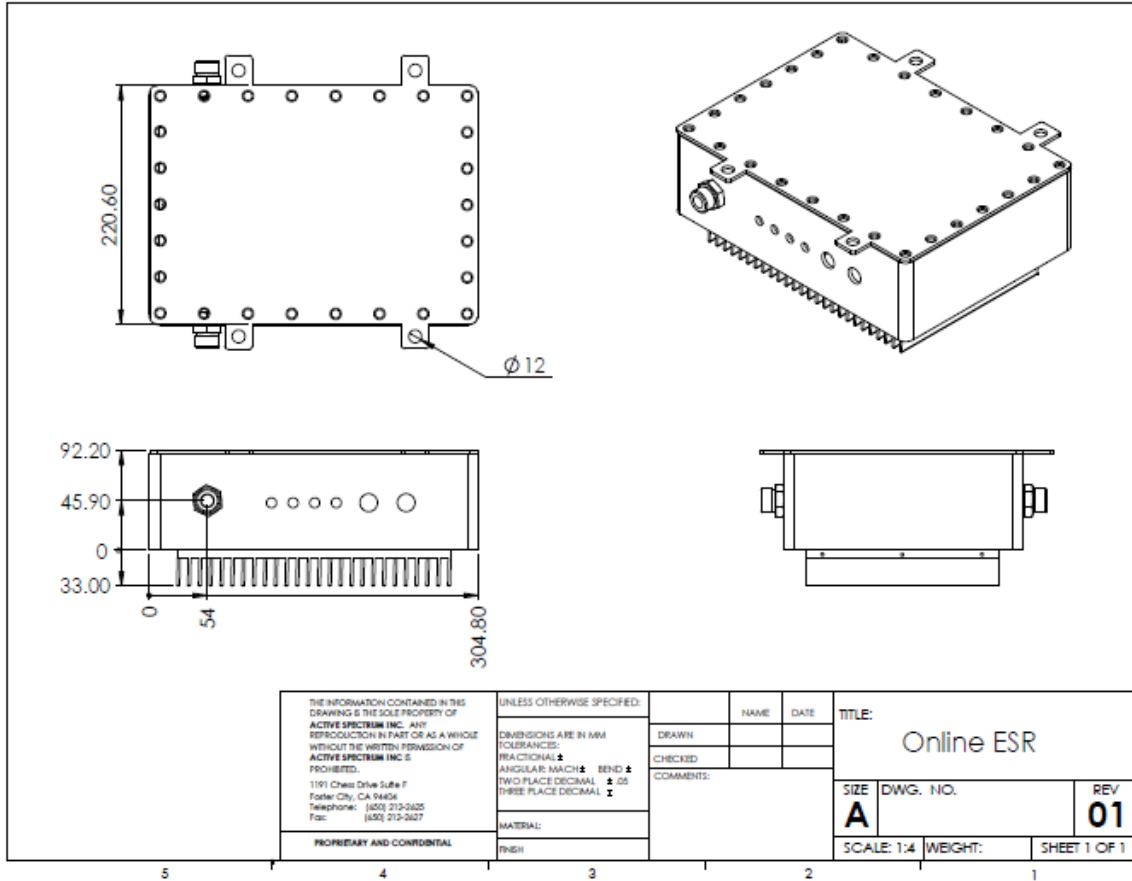
Magnet

Permanent Magnet	Samarium Cobalt
Center Field	3480 Gauss
Field Sweep Coils	+/- 150 Gauss
Modulation Coils	1.5 Gauss @ 43 kHz, 8-bit adjustable
Field Homogeneity	0.25 Gauss

Signal Processing

Computer	Fit-PC running Windows XP Embedded (Optional), 32 GB storage.
Software Options	Application specific software for quantification of oxidation, soot, vanadium, asphaltene and other quantities.

Outline Drawing: On-line X-band Micro-ESR



Hydraulic Oils and ASTM Correlation

Hydraulic oil samples from nuclear submarines were provided by the US Navy for analysis and comparison to ASTM-standard analysis techniques such as FTIR for measurement of oxidation. These oils are grade 2075 hydraulic oils (MIL-PRF-17672D).

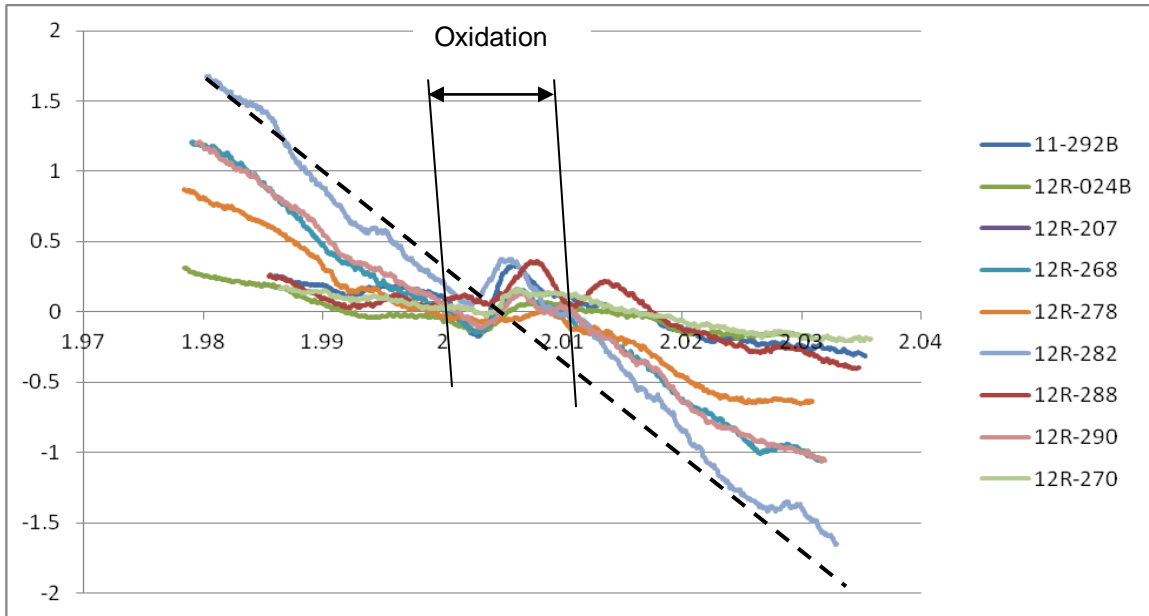


Figure 3: Oxidation and corrosion in hydraulic oils.

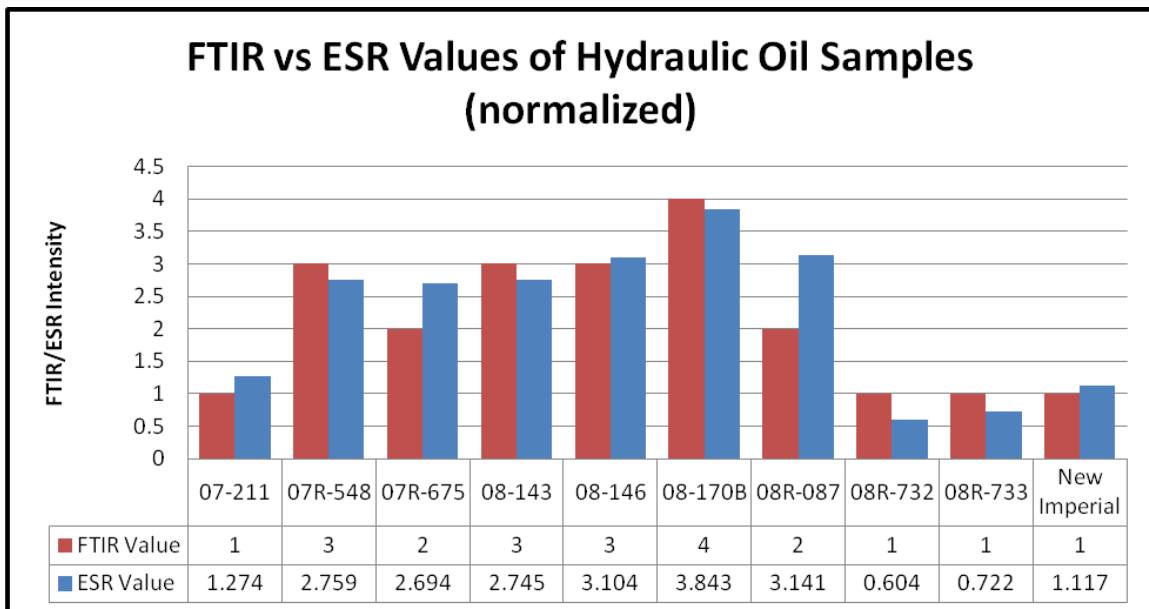


Figure 4: Comparison of ESR and FTIR ASTM D7414 analysis techniques.

Typical free radicals signals that we see in hydraulic oils are shown in Figure 3. The data show a narrow central line due to an organic radical, produced by oxidation processes. There is also a broad background line, which appears as a slope in these graphs. This broad line is due to iron oxides from ferrous corrosion in the hydraulic system. The peak height of the oxidation signal was compared to ASTM-standard FTIR measurements of oxidation performed by an outside lab. As shown in Figure 4,

Engine Oil

Several engine oils were tested by Micro-ESR. For gasoline engine oils, we observed a simple ESR peak due to thermal oxidation. The graph below shows our original results, for a field test conducted on a Honda sedan:

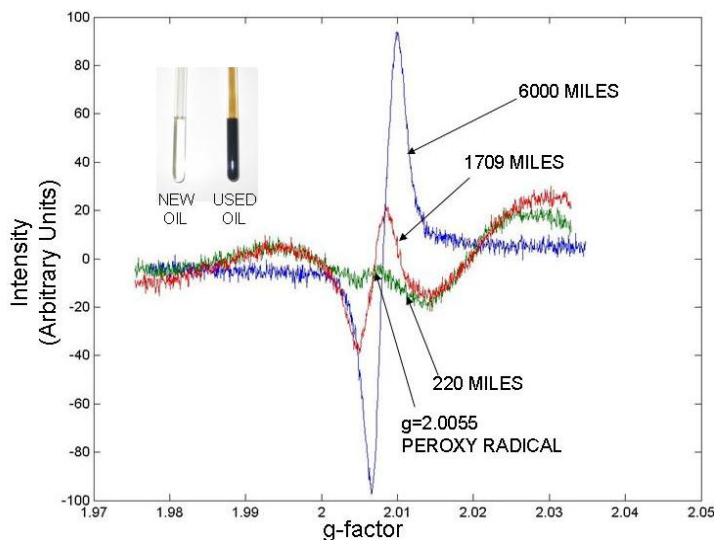


Figure 5: Field test of oxidation measurement by electron spin resonance spectroscopy.

In the gasoline engine field trial, a Honda accord with 2.4L gasoline motor was driven for 6000 miles without changing the oil or topping up. The increase in the oxidation free radical signal was measured over time using small (1 mL) samples withdrawn from the engine sump.

Additional testing was performed on diesel engines. Diesel engine oil often has a high concentration of soot, which creates a second, overlapping signal in an ESR spectrometer. Soot is strongly paramagnetic and can be detected using ESR spectroscopy in both liquids such as engine oils, and also in aerosol form as in diesel engine exhaust or in powder form (e.g. carbon nanotubes).

Measurements of % soot content correlate well between ESR and FTIR, as shown in Figure 6.

ESR Peak Height (scaled) vs Soot Percentage

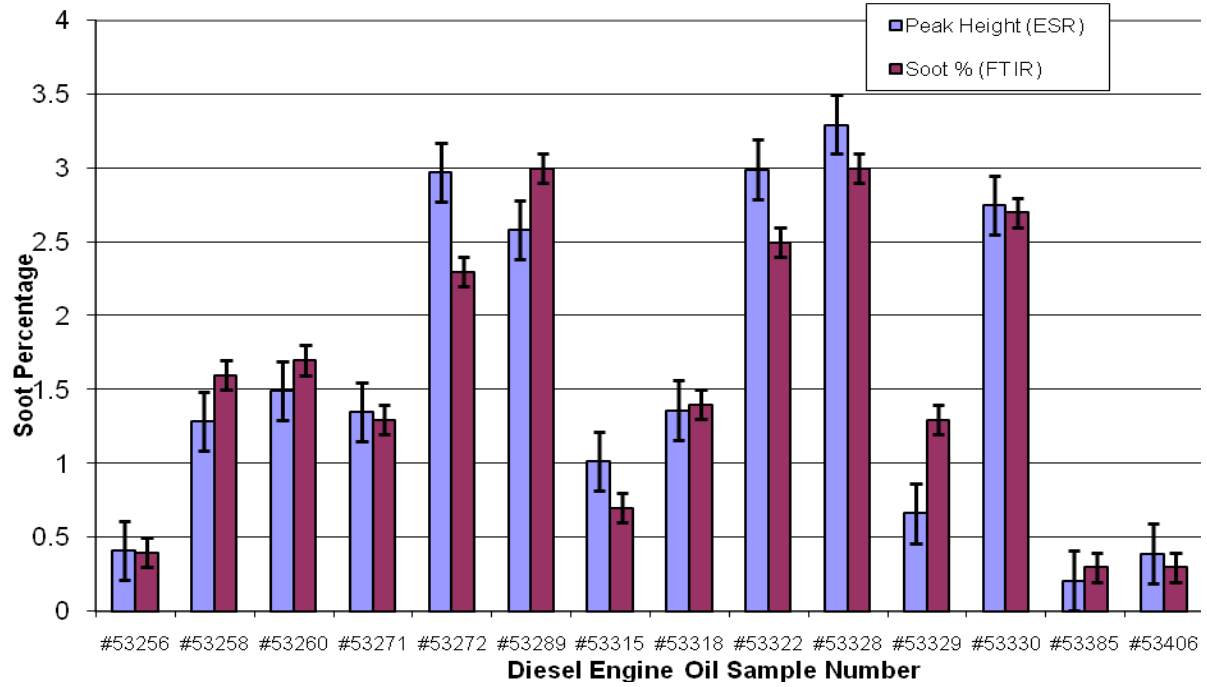


Figure 6: Correlation between ESR and FTIR measurements of soot in diesel engine oil.

Gearbox Oil and Thermal Coking

Gearboxes are a universal feature in many types of power transmission equipment. Ships, wind turbines and many other industrial machines have large gearboxes that are critical to operational readiness. In this set of experiments, we show the application of Micro-ESR to measure oxidation and, in a unique case, thermal coking of gearbox oils. Thermal coking is a unique and dangerous condition whereby the lubricant is degrading at such a rate and at such high temperatures that a large concentration of volatile gases can accumulate in the gearbox or other enclosed space. This accumulation of volatile gases has on occasion led to catastrophic equipment failures, including fires and explosions. Although rare, thermal coking related failures are often extremely expensive to repair.

In oxidized and coked gearbox oils, we see a buildup of the typical organic radical signal seen in other types of oil. In Figure 7, gearbox oils from two vendors were heated to 250°C for several hours. Unsurprisingly, these oils quickly degraded and precipitated a lot of heavy black sludge along with a large free radical signal.

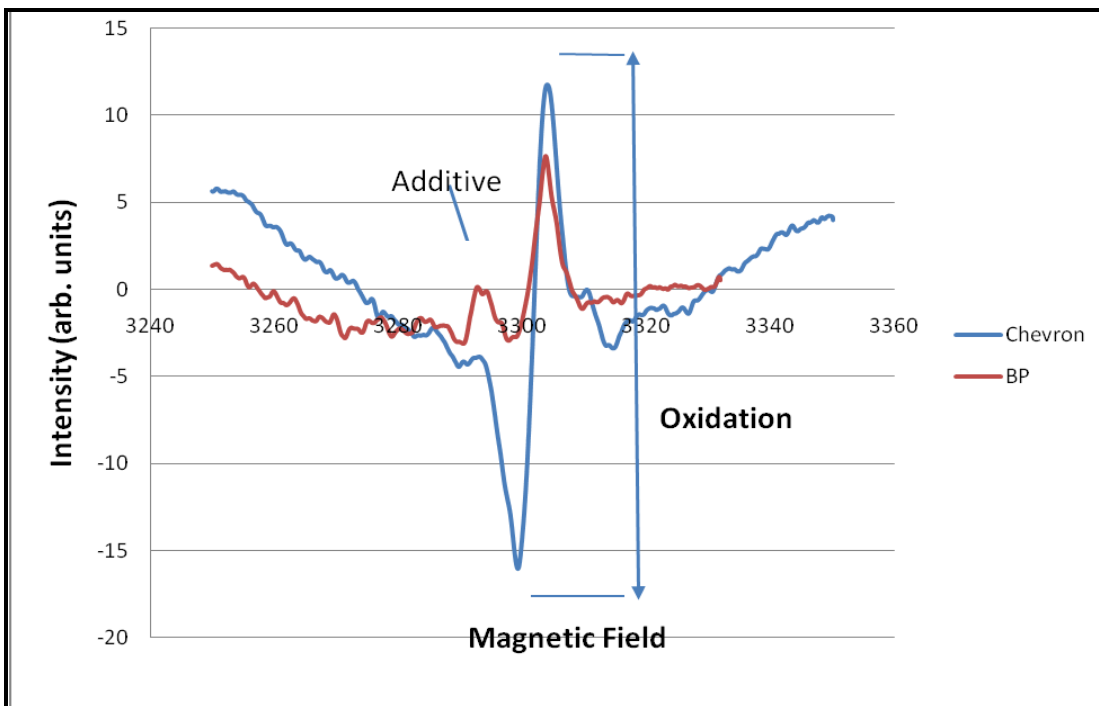


Figure 7: Thermal coking of Grade 2190 Gearbox Oils measured by X-band Micro-ESR

Subsequently, we used Micro-ESR spectroscopy to measure the degradation of gearbox oils in real time during heating. What is observed is a direct correlation between ESR signal intensity, and time and temperature. We also observe a direct correlation between ESR signal intensity and mass loss. Finally, we analyzed the headspace of the reaction chamber to determine the chemical composition of the vapor being emitted. For this, we used gas chromatography. The results of the GC

study showed conclusively that highly volatile byproducts were being released from the oils, which indicates that cracking and thermal coking were occurring in this case.

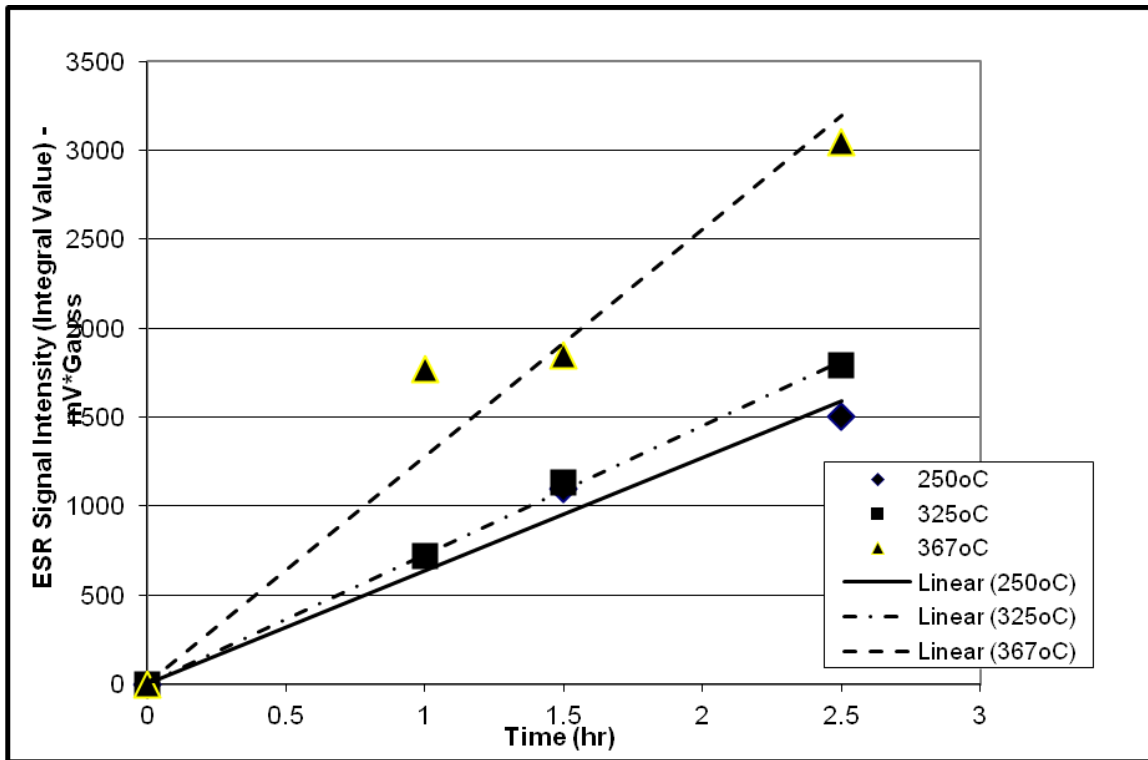


Figure 8: ESR Signal Intensity as a function of time and temperature.

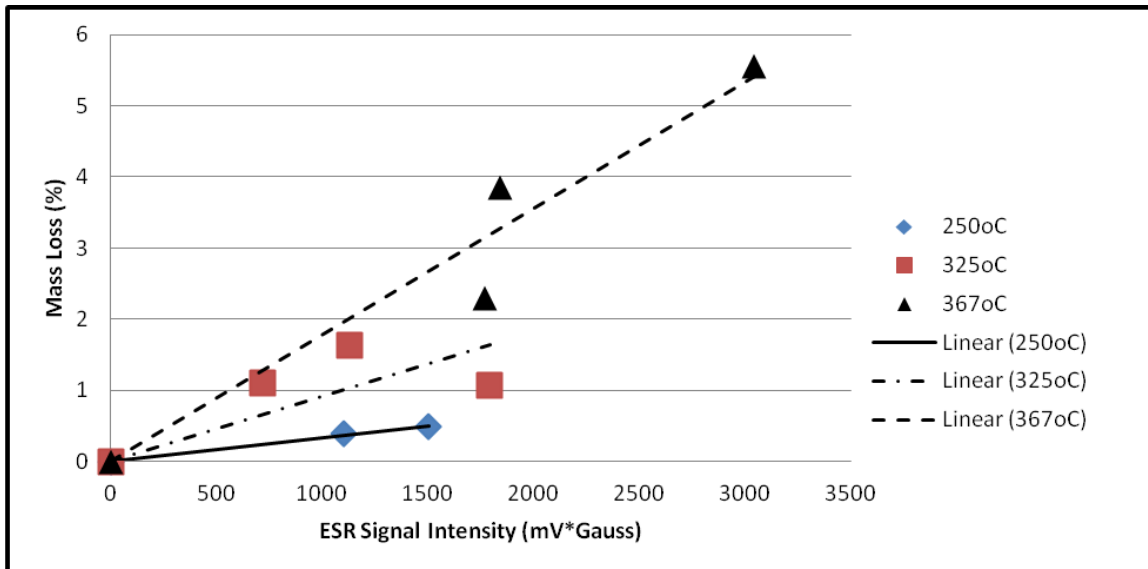


Figure 9: ESR Signal intensity as a function of mass loss during coking.

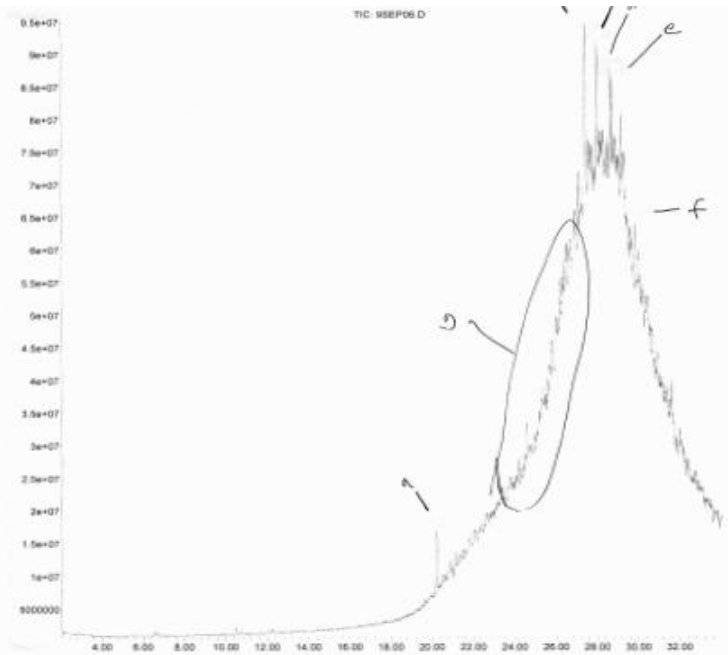


Figure 10: GC of New Gearbox Oil -- almost entirely long hydrocarbon chains (C29-C31).

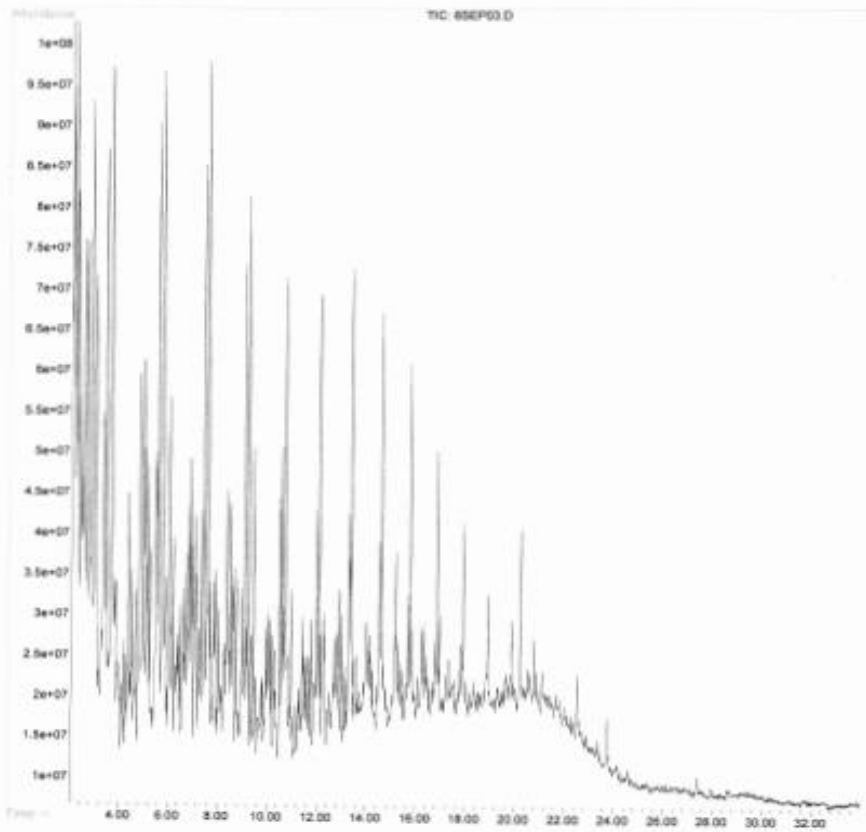


Figure 11: GC of headspace during thermal coking -- almost entirely volatile hydrocarbons.

Oil coked at 367 C for 2.5 hrs

Peak#	Ret Time	Area	Compound Name	Formula	% Area	Identity
1	2.088	1302939715	1,2-Dimethylcyclohexene	C8H14	2.84	Cycloalkane
2	2.2	1276335683	Cyclooctane	C8H16	2.79	Cycloalkane
3	2.282	1277709531	1,1,2-Trimethylcyclohexane	C9H18	2.79	Cycloalkane
4	2.549	1227087703	trans-7-Methyl-3-octene	C9H18	2.68	Branched Alkene
5	2.668	1623478268	3,3,5-Trimethylcyclohexene	C9H16	3.54	Unsaturated Cycloalkane
6	2.852	2176213988	4-Methyloctane	C9H20	4.75	Alkane
7	3	1440696963	3-Methyloctane	C9H20	3.15	Alkane
8	3.351	1077388759	m-Xylene	C8H10	2.35	Substituted Benzene
9	3.452	1631833179	1-Nonene	C9H18	3.56	Alkene
10	3.67	2688173298	n-Nonane	C9H20	5.87	Alkane
11	4.373	579560866	3-Methylnonane	C10H22	1.27	Branched Alkane
12	4.834	1983466799	1-Decene	C10H20	4.33	Alkene
13	4.979	1624799592	4-Methylnonane	C10H22	3.55	Branched Alkane
14	5.468	1272689728	1,2,4-Trimethylbenzene	C9H12	2.78	Substituted Benzene
15	5.581	2203848762	1-Decene	C10H20	4.81	Alkene
16	5.769	2184364495	1,2,3-Trimethylbenzene	C9H12	4.77	Substituted Benzene
17	6.026	1298477100	Nonyl-Cyclopropane	C12H24	2.84	Alkyl cycloalkane
18	7.437	1441420569	n-Undecane	C11H24	3.15	Alkane
19	7.595	2111178526	1-Dodecene	C12H24	4.61	Alkene
20	9.079	1155521705	n-Dodecane	C12H26	2.52	Alkane
21	9.217	1344061049	2,6-Dimethylundecane	C13H28	2.93	Branched Alkane
22	9.424	745287781	2-Methylnaphthalene	C11H10	1.63	Polycyclic Aromatic Hydrocarbon
23	10.492	639041459	1-Tridecene	C13H26	1.40	Alkene
24	10.573	559027289	n-Tridecane	C13H28	1.22	Alkane
25	10.699	1143733903	1-Heptadecene	C17H34	2.50	Alkene
26	12.078	1785600707	n-Tetradecane	C14H30	3.90	Alkane
27	13.373	2051489367	n-Pentadecane	C15H32	4.48	Alkane
28	14.595	1612694760	1-Hexadecene	C16H32	3.52	Alkene
29	15.753	1094682600	n-Nonadecane	C19H40	2.39	Alkane
30	16.855	977862257	n-Octadecane	C18H38	2.14	Alkane
31	17.905	710879562	n-Nonadecane	C19H40	1.55	Alkane
32	18.907	437265968	n-Eicosane	C20H42	0.95	Alkane
33	19.87	255179150	HENEICOSANE	C21H44	0.56	Alkane
34	20.233	624408343	phenyl-naphthyl-amine	C16H13N	1.36	Anti-Oxidant
35	20.79	239550994	n-Docosane	C22H46	0.52	Alkane

Figure 12: Detailed composition of headspace during thermal coking.

Finally we ran tests to compare ESR signal intensity with flash point as determined by ASTM D91. Not surprisingly, flash point does not correlate very closely with oxidation. In the initial period, some low volatility additives are still present in the oil. As oxidation proceeds, these lower volatiles evaporate or dissipate and what is left is a large volume of long hydrocarbon chains with high flash points. Only in the event of thermal coking does the flash point of the residual oil (but not the headspace vapors – they evaporated prior to testing in this case) rise beyond the level seen in normal use.

In practice, this data shows the power of an on-line oil condition monitoring system to detect the rapid onset of dangerous breakdown conditions in a piece of critical machinery. The degradation observed in these studies occurred in a matter of just two hours. An offline measurement and sampling protocol would never detect an emergent event like this in time for the equipment operator to take corrective action.

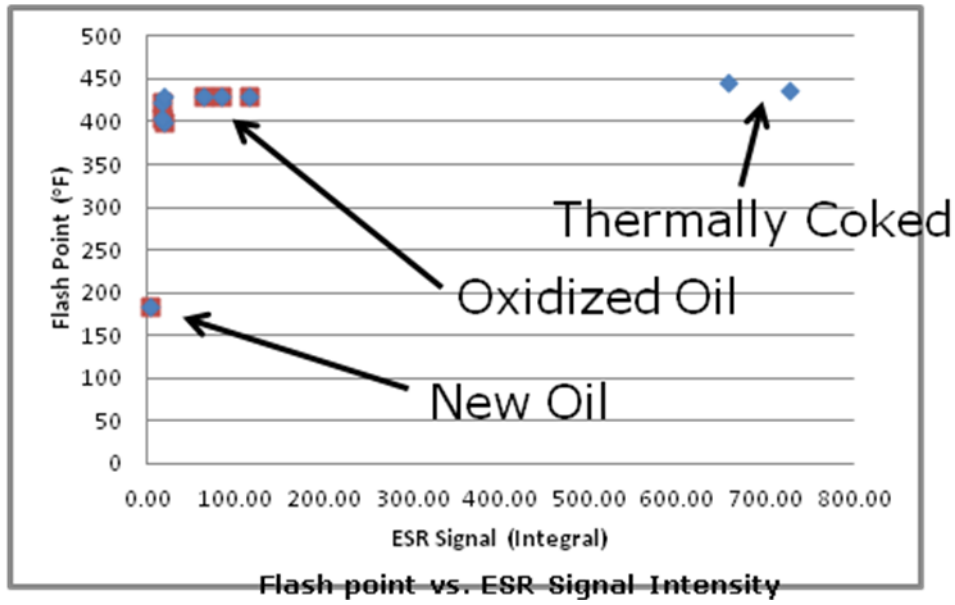


Figure 13: Comparison of ESR signal intensity and flash point by ASTM D91.

Marine Lubricants: Residual Fuel Dilution

Contamination of marine engine lubricants by heavy fuel oil is a common problem with medium speed diesel engines. A unique test for residual fuel dilution was developed by ExxonMobil in the late 1980s. This test measures the vanadium in unburned heavy fuel oil. Vanadium occurs naturally in many crude oils and residuals in the form of vanadyl porphyrin. When burned, the vanadyl porphyrin turns to vanadium oxide, which is not ESR visible. Vanadyl porphyrins, by contrast, along with asphaltenes, both have unique, readily identifiable signals that can be measured by Micro-ESR technology.

Minimizing the rate at which lube oil is replenished in the sump can in turn reduce engine operating costs. The typical setpoint is to adjust the rate of oil replenishment to keep the unburned fuel concentration in the oil at 0.5% or less. Using on-line Micro-ESR technology, this can be done in real-time, with closed-loop feedback control of the oil pump. Cost savings are obtained both by minimizing consumption of lubricants, and in avoiding sludge buildup in the engine.

We studied a series of marine lubricants with varying percentages of raw fuel dilution. The figure below shows the results, in which the ESR spectra of vanadyl porphyrin and asphaltene are clearly visible in the marine lubricant.

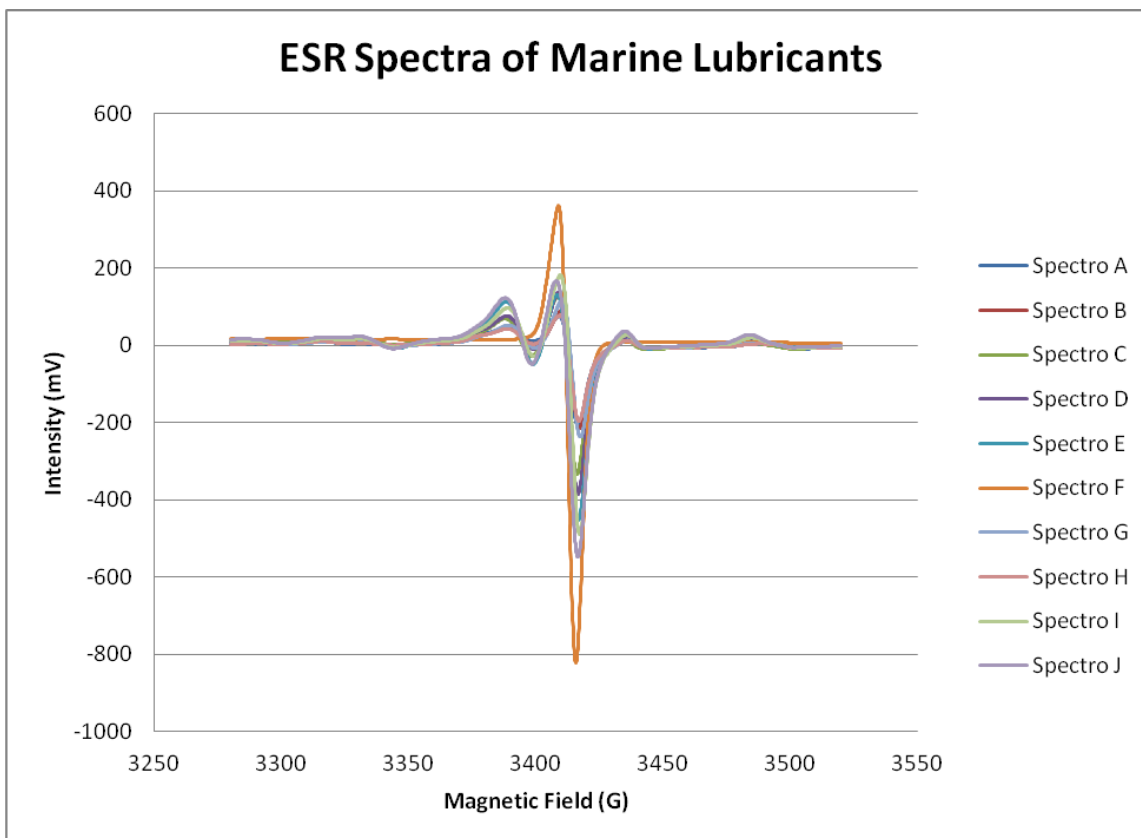


Figure 14: ESR Spectra of Marine Lubricants showing unburned fuel dilution.

The ESR results were quantified and compared to raw fuel dilution measurements performed using precipitation, which is the conventional approach.

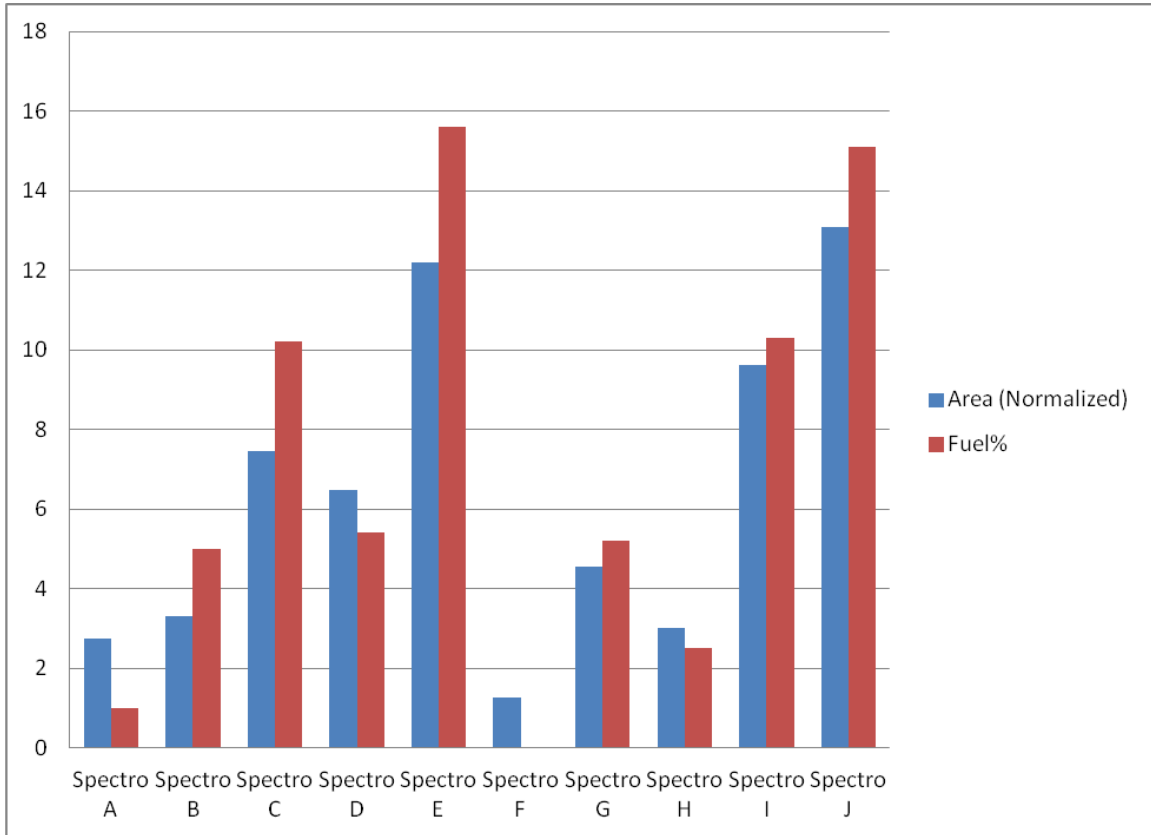


Figure 15: Vanadyl porphyrin signal intensity compared to precipitation measurement.

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 or electrical properties of the oil (dielectric constant, viscosity, electrical impedance, etc.) and then try and relate that data to underlying chemical changes. 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.

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, automated, on-line condition-based maintenance.

Table of Sample Applications

Application	X-band Micro-ESR
Crude Oil Analysis	X
Marine Fuel Dilution of Lube Oil	X
Soot and Water in Lube Oil	X
Oxidation of Lube Oil	X

Oxidation of Hydraulic Oil	X
Thermal Coking of Lubricating Oils	X
General Lab Use	X
Irradiation of Food and Plastics	X
Educational Uses	X

Availability

ASI's high sensitivity X-band Micro-ESR System is available worldwide either directly from Active Spectrum Inc. or through our distribution partners:

In the Netherlands, Germany and surrounding countries:

Dennis Hoogendonk
Omnitek BV
Meridiaan 40
2801 DA Gouda
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Phone: [+31-\(0\)182-302990](tel:+31-(0)182-302990) Fax: [+31-\(0\)182-302999](tel:+31-(0)182-302999)
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