

### **Summary**

This application note describes the evolution of free radicals in engine oil due to normal usage in a conventional gasoline engine. It also discusses briefly the process for sampling and determining the free radical content in engine oil through electron spin resonance.

### **Background**

Free radicals are highly reactive uncharged atoms or molecules that arise as a result of unpaired valence electrons. Radicals are deliberately used in chemistry, frequently occur during irradiation of materials, and have been implicated in the aging process in biology. They are also commonly produced through combustion and oxidation in the lubricating oils of internal combustion engines run at high temperatures and speeds in the presence of oxygen. They can therefore be used as a marker for age in the oil, and potentially stability and efficacy of the lubricant. These molecules can be readily detected using the technique known as Electron Paramagnetic Resonance (EPR).

In EPR (or Electron Spin resonance, ESR), a static magnetic field forces the two spin states of an unpaired electron to enter different energy states. Microwave electromagnetic radiation is then absorbed at characteristic frequencies to yield an indicator of the presence of the radical. In a wrinkle to the technique, the presence of adjacent atoms also cause a magnetic field, resulting in “hyperfine splitting” and a characteristic fingerprint for the radical molecular structure. The total absorbance signal is related to the total number of radicals present.

In most synthetic engine oils, there are antioxidants added to react with any radicals formed increase the longevity of the oil. However, antioxidants are often consumed over time, reacting with the free radicals and stabilizing them. Often this reacted antioxidant is itself a radical, although a more stable one than the original oil product. As a result, radical concentrations and types can evolve with time. If unchecked, these radicals can lead to polymerization or scission of the lubricant molecules, both of which will result in degraded lubrication performance. Most consumers and manufacturers are aware of this issue, which is one reason why oil changes typically occur around 5000 miles.

### **Procedure and Results**

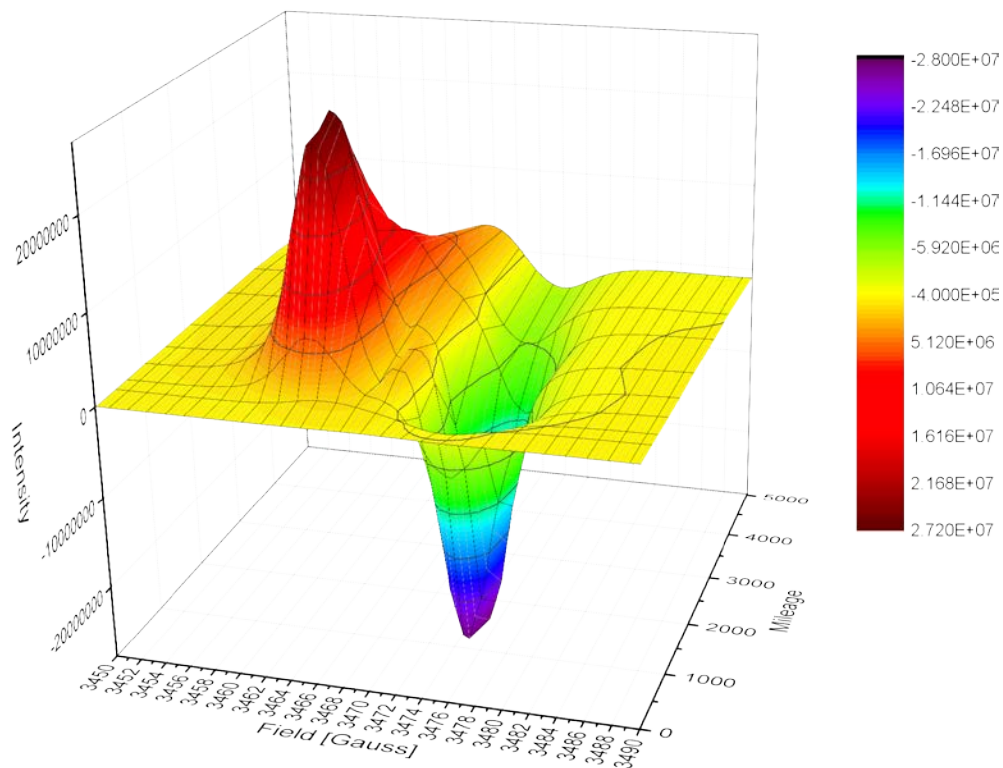
Engine oil was extracted periodically from a moderate mileage modern 6-cylinder Infiniti gasoline engine after a fresh oil change. The engine oil is analyzed by the EPR spectrometer to monitor the evolution in free radicals as the vehicle accumulates mileage. A small aliquot of fresh oil was tested as a control before testing aged samples. A sample of oil was taken every 500-1300 miles to quantify the changes in concentration and type of free radicals in the oil. In the initial control oil, no radicals were observed. At 400 miles, an initial peak in the ESR spectra was observed at a field strength of 3467 Gauss (Figure 1 and Figure 1). This peak shifted to lower field strengths as the oil aged until at 1500 miles there was a pronounced peak at 3464 Gauss with a secondary peak at about 3469 Gauss. This behavior likely indicates generation of one kind of radical that is gradually converted to a secondary radical, either on the antioxidant, or elsewhere, and is more clearly seen in Figure 1, where the individual peak heights are tracked at specific field strengths, effectively mapping the evolution of the radicals with time. This maxima in the spectrum then falls and shifts back towards the original peak observed at low mileages.

The area under the curve in the resonance spectrum is directly proportional to the number of spins in the sample. One can therefore determine directly from the spectra, and a knowledge of the sample mass the total number of spins present in the specimen. Figure 1 presents the evolution over time of the total free radical concentration in the sample. As observed qualitatively before, the radical concentration increases quickly at low mileage and then masses through a maximum. At about 3500 miles the total concentration appears to have stabilized, although further measurements would be required to verify this observation. This observation may indicate a rapid growth in radicals until sufficient levels are built up to begin to react favorably with the antioxidants present in the system. Over time, one might expect to eventually see even these values change as the system exhausts the antioxidants present.

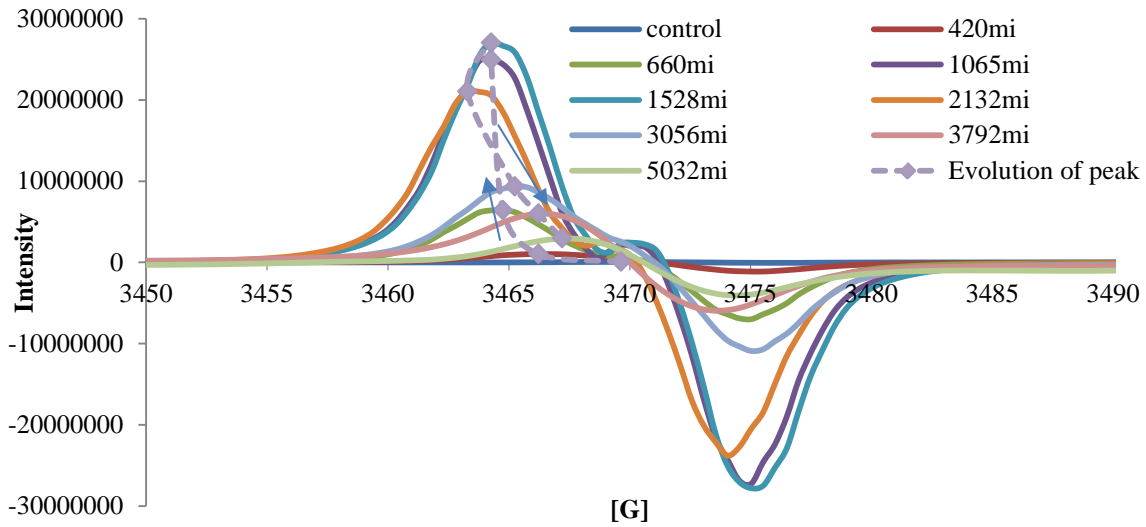
These observations may indicate the activity, and eventual consumption, of the antioxidant package in the oil. To attempt to clarify the source of this behavior, FTIR analysis was performed comparing the high mileage oil to the control samples (Figure 2). Although generally the spectra is unchanged, there are a handful of locations where peaks disappear in the aged oil compared to the control sample, suggesting chemical changes in the lubricant. Comparing the aged sample against a library of FTIR spectra (Figure 3) yields a good match for a conventional lubricant,

### Conclusions

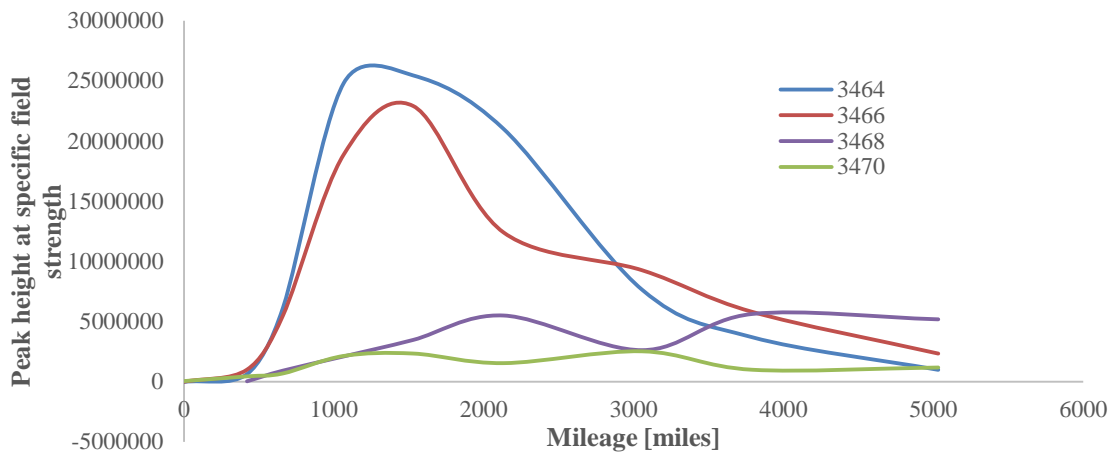
The data presented here emphasizes the utility of ESR in a range of possibly applications. Although conventionally used as an analytical tool in radiation chemistry it can find usage in other areas where the presence of radicals may be detrimental, or may be desired, such as in radical chemistry. In the short study discussed here there is clear evidence of generation, and then evolution of radicals in the oil, most likely as a result of initial creation, and then conversion with antioxidants or reaction to more stable forms. As a tool for examination degradation of these materials ESR clearly has substantial utility, particularly when used in conjunction with other, more conventional techniques.



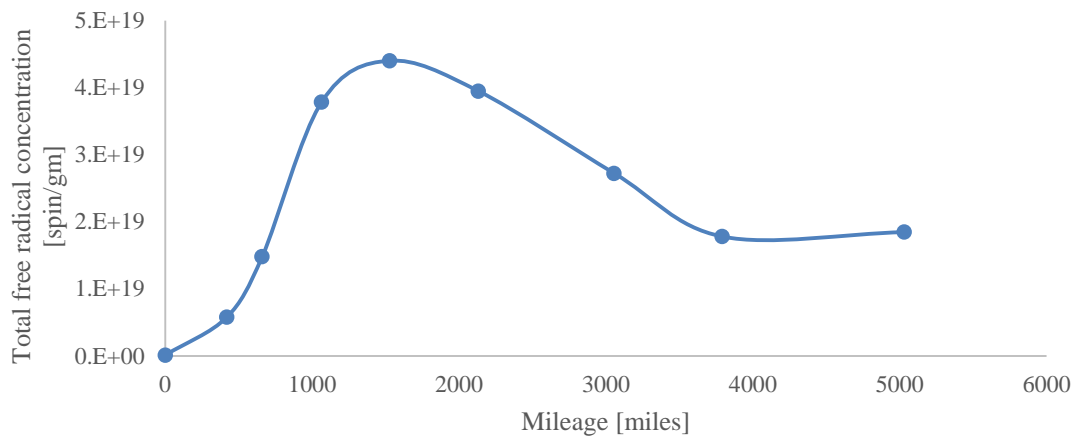
**Figure 1: EPR Intensity Graphs for control (0 mi), 420 mi, 660 mi, 1065mi, 1528 mi, 2132 mi, 3056 mi, 3792 mi, 5032 mi.**



**Figure 2: EPR Intensity Graphs for control (0 mi), 420 mi, 660 mi, 1065mi, 1528 mi, 2132 mi, 3056 mi, 3792 mi, 5032 mi. Dotted line indicates evolution of primary peak.**



**Figure 3: Signal intensity at specific field strengths plotted against mileage. These changes in intensity are related to the evolution in radical types.**



**Figure 4: Free radical concentration plotted against mileage (scaled to highest radical concentration).**

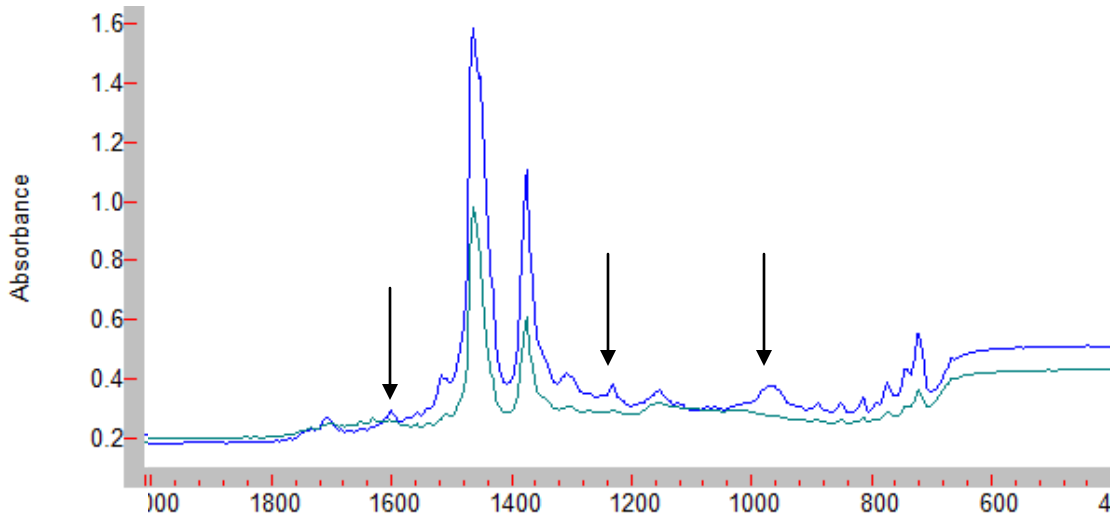


Figure 5: FTIR New Oil (control) vs. Used Oil (5032mi) showing peak degradation. Blue line new oil, green line used oil. Arrows indicate loss of peaks from the new oil after aging.

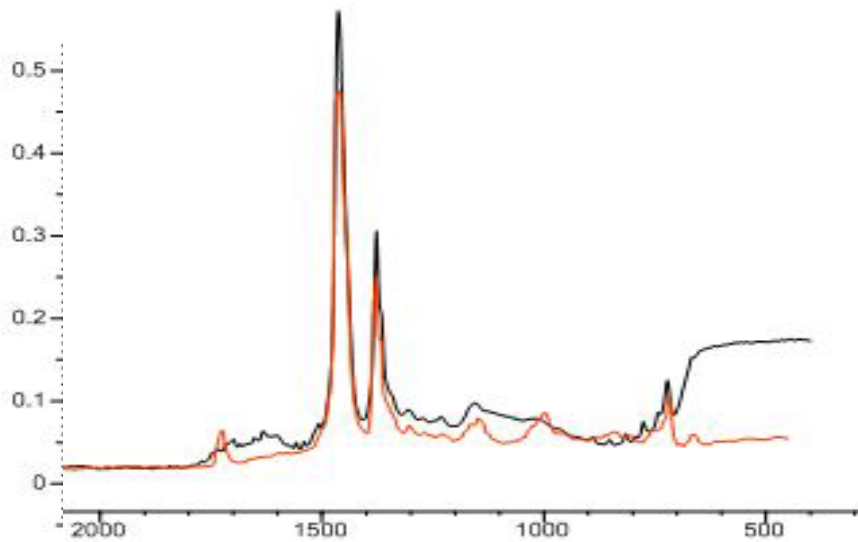


Figure 6: Used Oil (5032mi) Library Match to “super permalube” (orange spectra).