



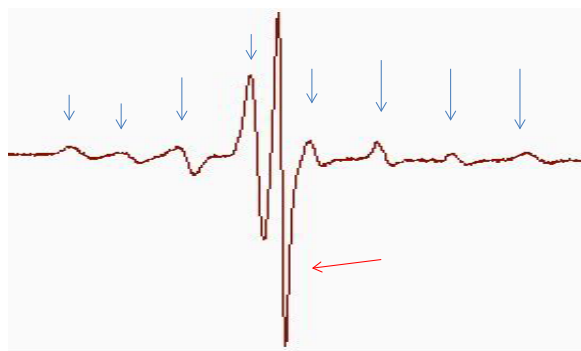
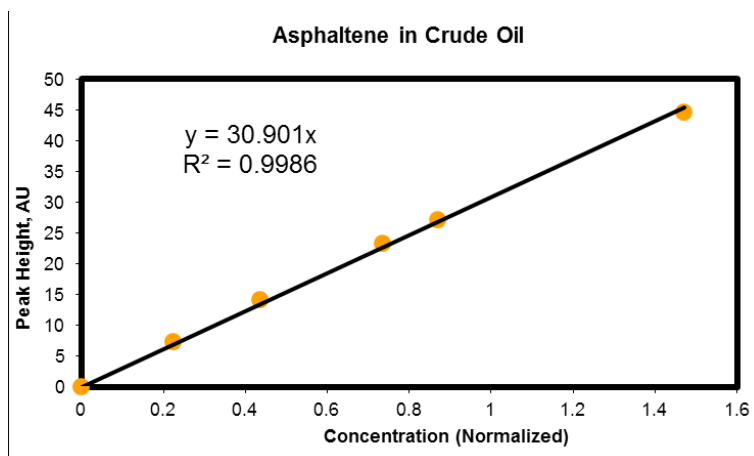
Asphaltenes and microESR

The ESR signal of an asphaltene in crude oil.

(Figure 1) The eight blue arrows are pointing to the signal from ^{51}V in vanadyl porphyrin. The red arrow is pointing to the organic asphaltene radical. All asphaltenes have the organic radical. The amplitude of the organic radical corresponds to the

concentration of asphaltene in the sample. Not all asphaltenes contain vanadium, but a large number do.

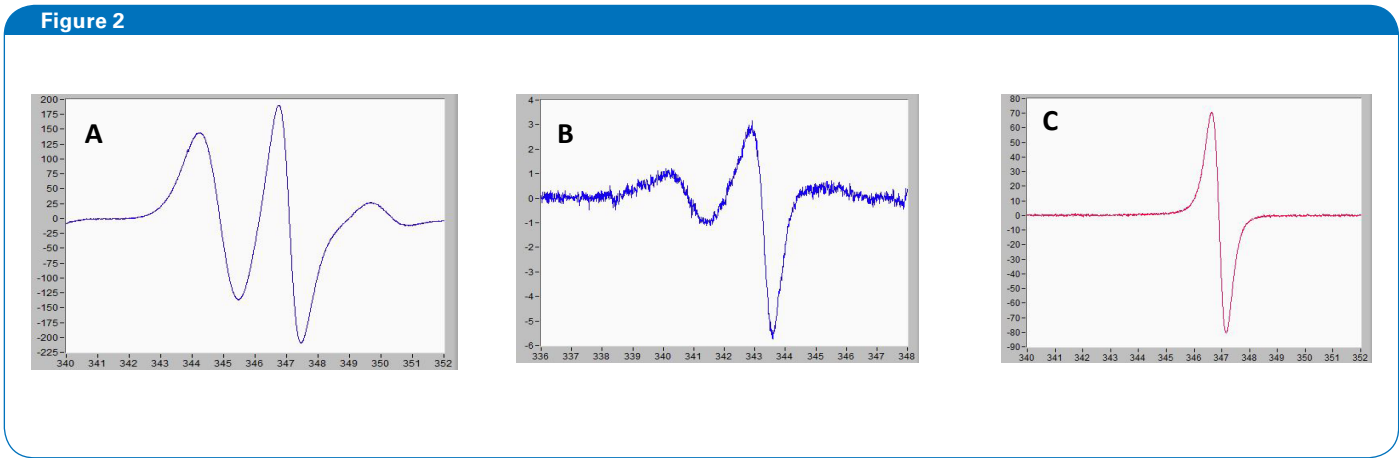
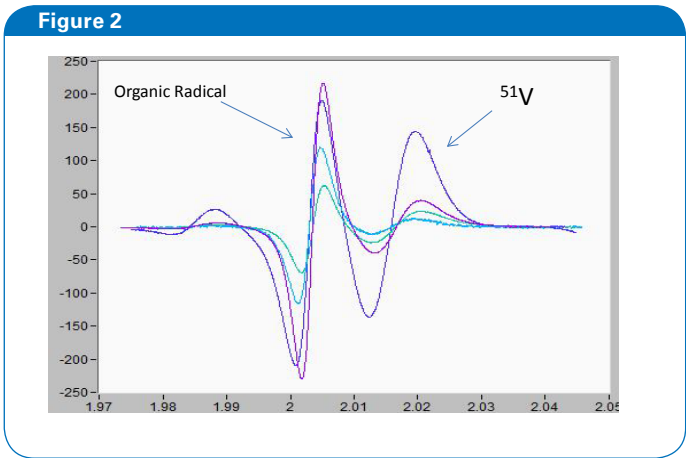
Figure 1



Examples of Asphaltene ESR Spectra

The overlaid spectra to the right (figure 2) are of other crude oil samples. Note the huge variation in signal amplitude as well as the variation in the asphaltene: vanadyl radical. The vanadyl peak is on the right in these spectra as they are displayed in g-factor rather than gauss. The g-factor parameter is frequency independent.

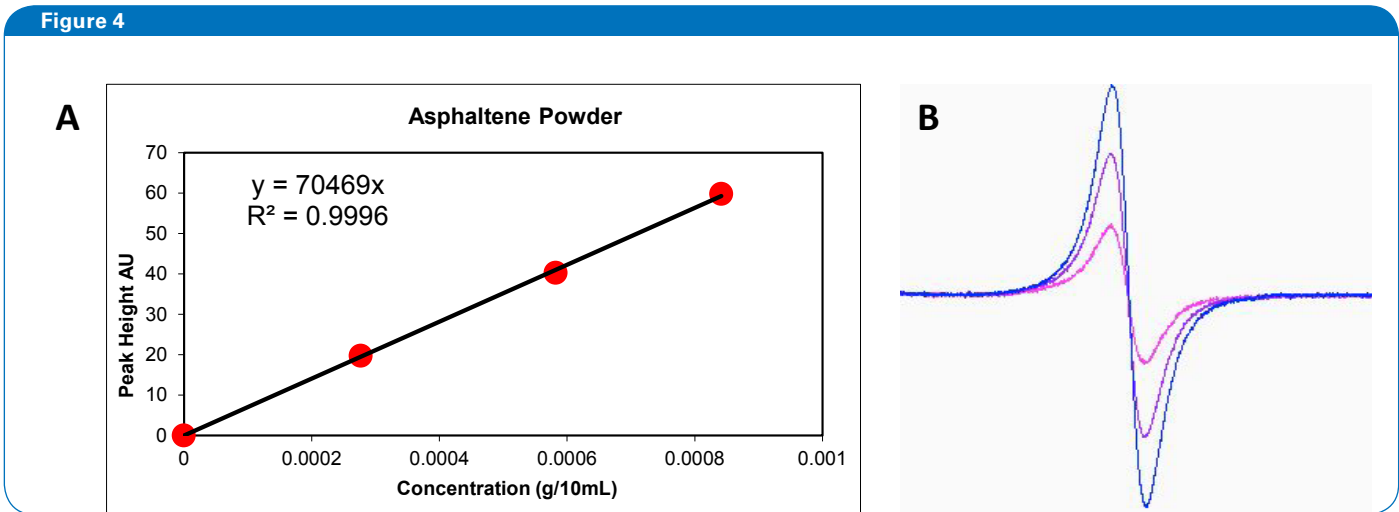
The below are the ESR spectra of several different asphaltenes. (Figure 3) Note the large vanadyl signal in A. Spectrum B has a vanadyl signal, but note how small the signal amplitude is (scale on left). The asphaltene in spectrum C has no vanadyl peak.



Asphaltene Concentration by ESR

Asphaltene concentration can be easily measured by ESR once a calibration curve has been made. (figure 4) (A) is the calibration curve made using an asphaltene powder dissolved in toluene. (B) The ESR spectra of the various concentrations

of asphaltene powder used to make the calibration curve. Active Spectrum has software that will automatically measure the concentration of an unknown sample once the calibration data has been entered.

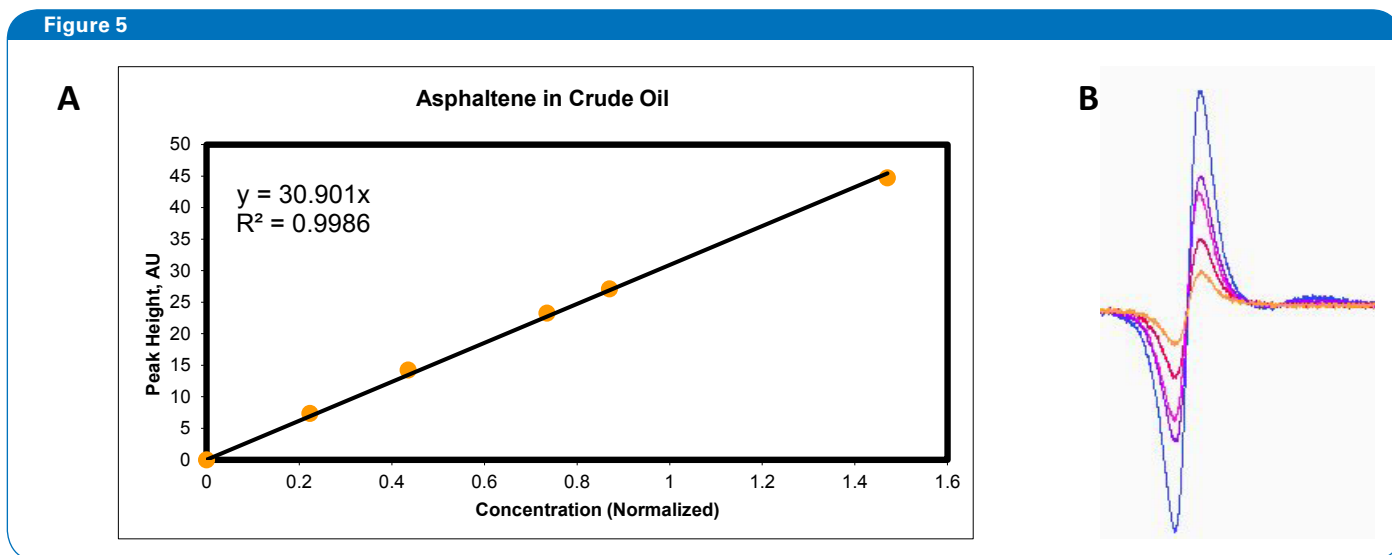


Asphaltene in Crude Oil

A known mass of crude was diluted to 10 mL in toluene. (A) shows the normalized mass of crude vs the peak to peak amplitude of the ESR signal. (B) The spectra of the diluted crude oil samples. Once a calibration curve has been made, the

concentration of other unknown samples* can be automatically determined with either Active Spectrum's acquisition or offline processing software.

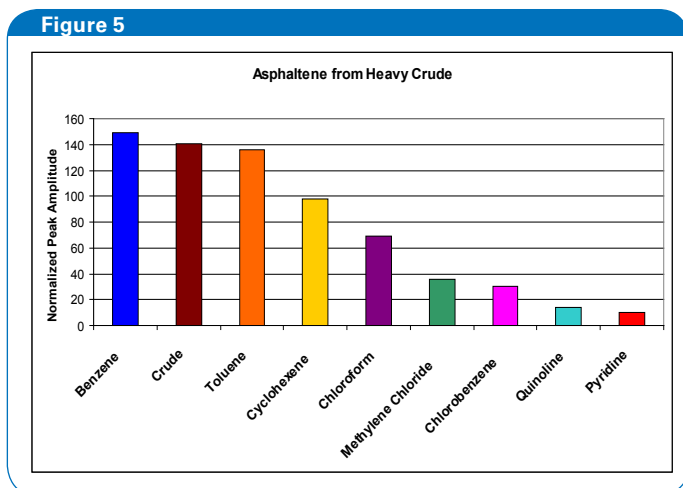
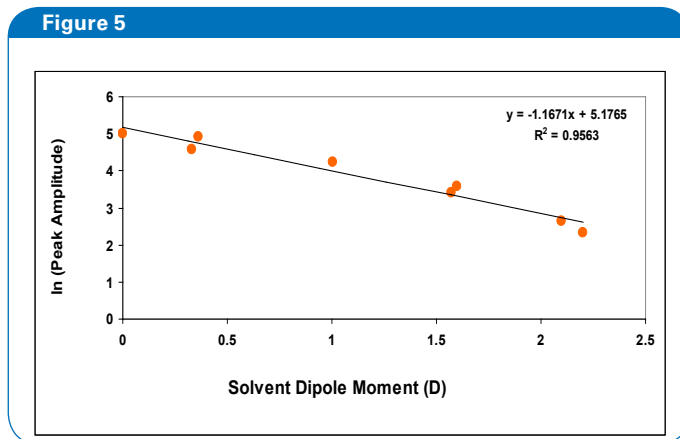
*This will work well with crude from the same geographic region.



Asphaltene Radical Concentration and Solvent Polarity

The radical signal for several different heptane precipitated asphaltenes in different solvents was measured by ESR. It has been previously noted that the radical signal decreases exponentially with increasing solvent polarity [1].

The chart to the right is a log plot of relative radical concentration of asphaltene in various solvents as a function of solvent polarity. The slope of plots for all asphaltenes tested was about -1.1.



The chart to the left illustrates relative radical concentration for the dissolved asphaltene in various solvents. The signal of the crude from which the asphaltenes was precipitates is also included.

[1] K.C. Khulbe, et al, *Fuel Processing Technol*, **32** (1992) 133-141

Asphaltene Radical Stability

- The polarity of the solvent certainly influences asphaltene radical stability, but aromaticity is also an important factor.
- Cyclohexene has a slightly lower dipole moment than does toluene; however, the asphaltene radical concentration is higher in toluene.
- Benzene, both aromatic and with zero dipole moment, gives the largest signal.
- Cyclohexane also has zero dipole moment, but the asphaltenes are not completely soluble in cyclohexane. Asphaltanes are completely soluble in cyclohexene which has a dipole moment of 0.331 D.
- A 0.3 M solution of naphthalene in benzene also has zero dipole moment, and supports the same radical concentration that neat benzene does. Doubling the concentration of naphthalene in the solution causes an 42% decrease in signal intensity.
- A 0.85 M solution of phenol in benzene lowers the signal intensity 21%. Phenol has a dipole moment of 1.7 D.
- Chlorobenzene has a dipole moment of 1.56 D, very similar to aniline, 1.52 D. Both compounds are also aromatic, so it could be expected that the concentration of radicals for a given asphaltene would be about the same in both solvents. Unexpectedly, the asphaltenes are not soluble in aniline. It is noted, however, that the dipole in aniline is toward the aromatic ring, and the dipole in chlorobenzene points away from the aromatic ring

Figure 6

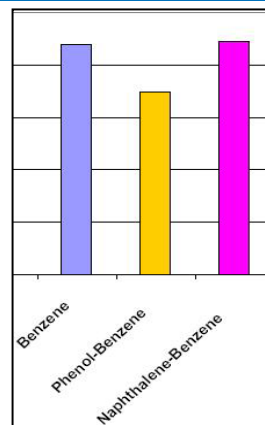


Figure 7

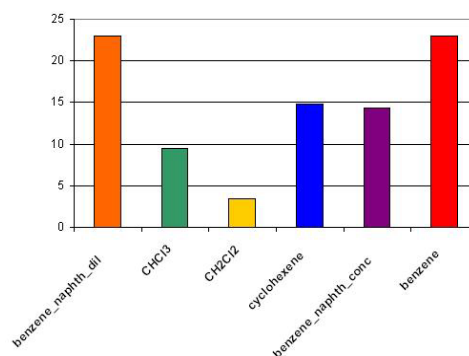


Figure 8

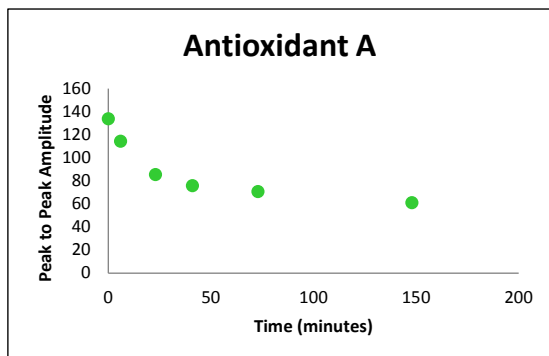
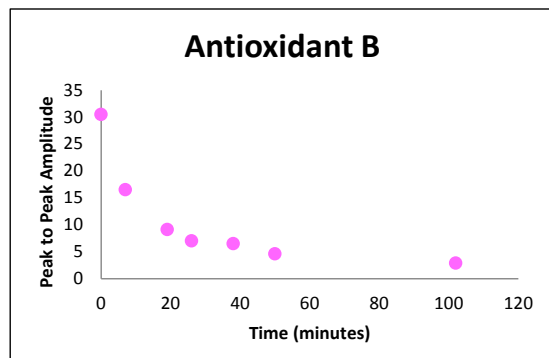


Figure 9



Elucidate Reaction Mechanisms

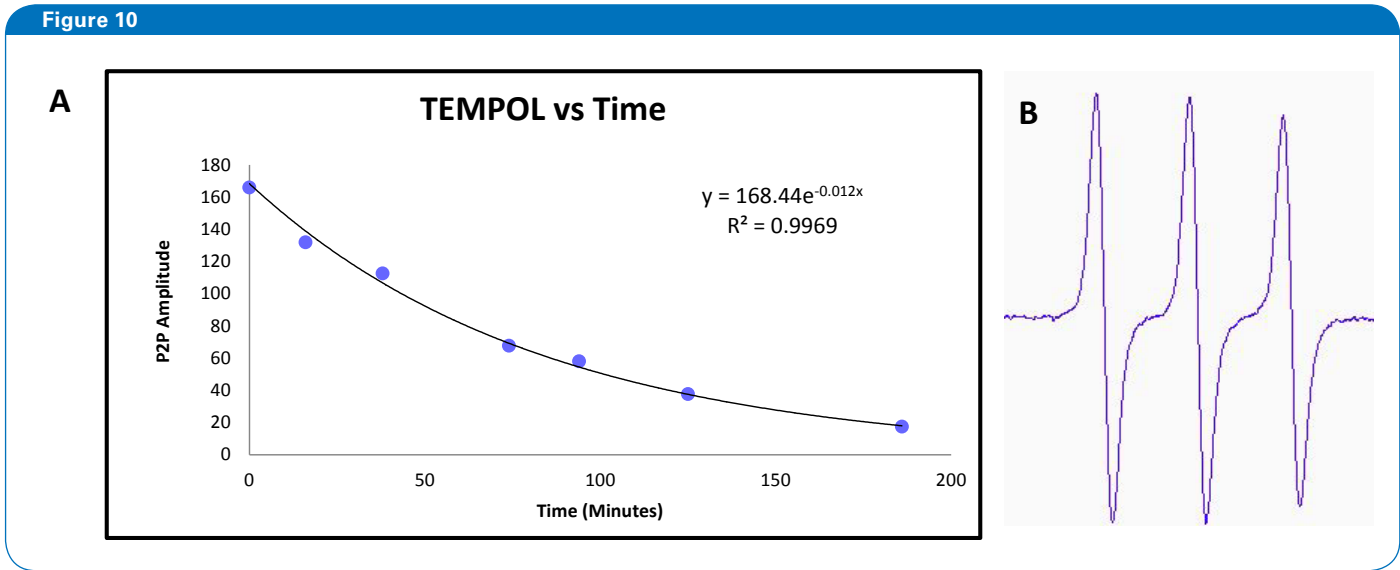
Monitoring process additives can also give insight into elucidating reaction mechanisms involving radicals. In both the above reactions, the peak to peak amplitude of TEMPOL was monitored over time. Both reactions exhibit competing processes.

Nitroxides are stable radicals, and are often used to monitor, or as process additives as they are easy to follow with ESR. Galvinoxyl (right) is another stable radical that can be used for the same purpose. Galvinoxyl, however, has a distinctly different ESR signature.

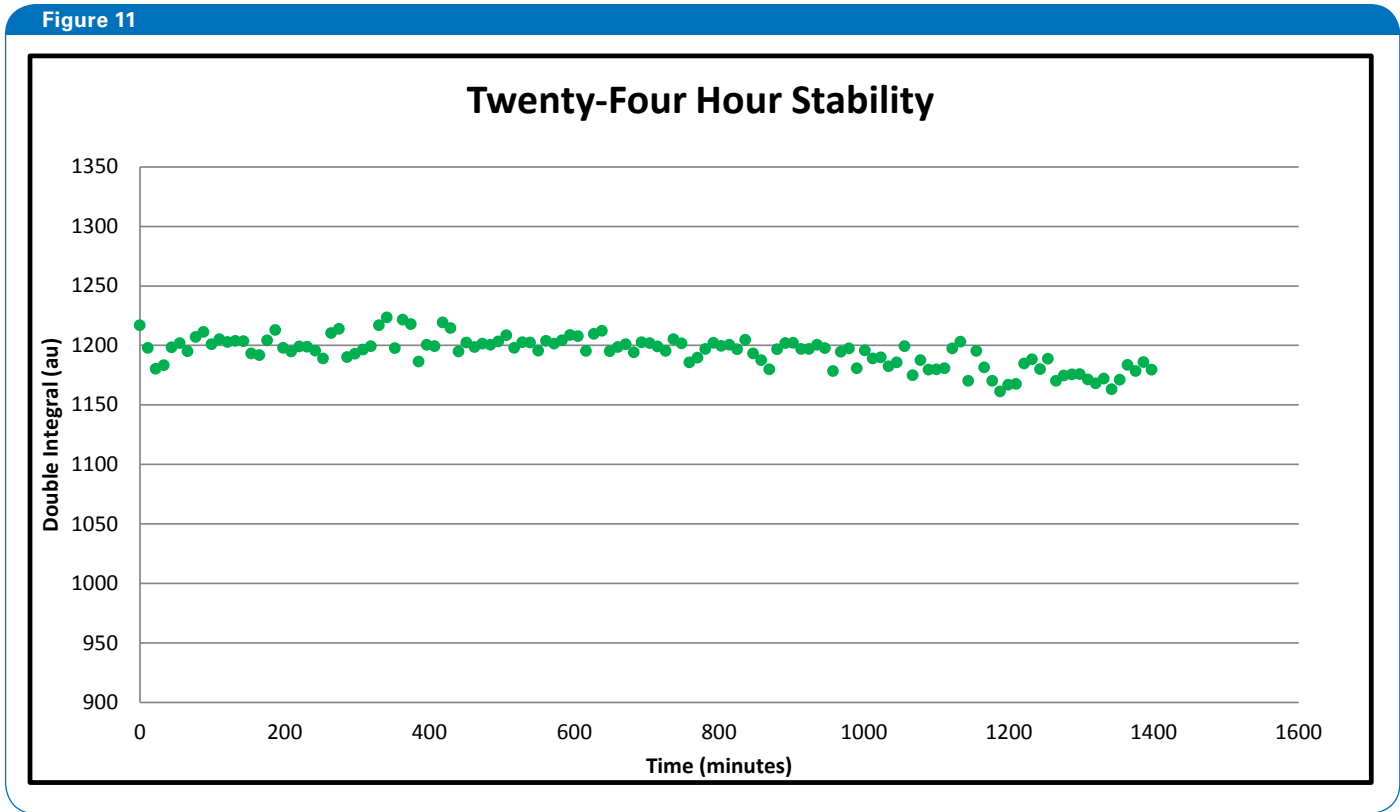
Monitor Process Additives in Real Time

Process additives can be easily monitored in real time. The above chart (A) shows the peak to peak amplitude of the nitroxide, TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl), over time when added to a solution of mineral oil with

an amine antioxidant additive. This reaction follows nice, first-order kinetics. (B) The ESR spectrum of TEMPOL. Nitroxides all have a three line spectrum because the unpaired electron is localized over the ^{14}N . The coupling to the nitrogen splits the spectrum into three lines.



Stability:



Double Integral values within 0.7% over four hours

Double Integral values within 1% over twenty-four hours

References

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