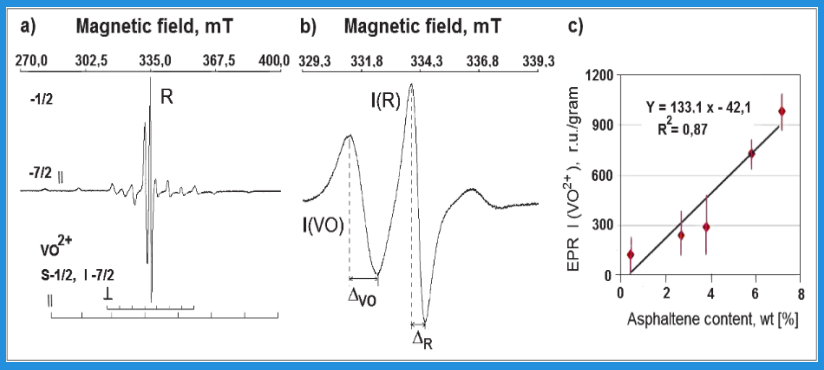
EPR-spectroscopy in petrochemistry

Oil production and processing is one of the most crucial industries, which is basic in production of numerous vital products. The problem of oil purification and of its deeper processing as well as of its responsible consumption is still actual in spite of the development of alternative energy sources. At the same time, the ecological consequences of soil pollution with oil and oil products require new methods of pollution control and new ways of pollutants deactivation along with oil products recycling.

Along with various methods of physicochemical analysis, the EPR method has a number of practical applications in the oil and oil refining industry due to its high information content and the ability to detect, identify and quantify the content of impurities and to judge their localization (structure and environment), and monitor reactions caused by free radical processes.

EPR-research allows to monitor: the starting point of machine lubricating oils thermal destruction; coke formation processes; chemical additives concentration; transition elements concentration; oxidation and polymerization processes, degree of oil photodegradation. EPR-spectroscopy can be utilized for determining the pollution degree of lubricating oils with fuel during the ship engine operation. By using the EPR technique the mechanisms of oil and its components (aromatic hydrocarbons, bitumens and asphaltenes) oxidation reactions are being researched and their kinetic models are being built, aiming to develop the chemical ways of initiating the raw oil oxidation process mediated by various chemical additives as well as to suppress the oxidation processes if needed.



The EPR method was used to study the aggregation of asphaltenes in model solutions and crude oil. The signals of free radicals (R) and paramagnetic centers of the vanadylporphyrin VO2+ complex were recorded on X-band EPR spectrometer CMS 8400. The connection of EPR signals with asphaltenes is confirmed by their decrease when diluting crude oil with maltenes.

The samples of synthetic engine oil available on the market have been studied for demonstration of EPR method in studying the process of free radicals production in engine oil. After changing the oil in the engine with a fresh one, a periodic sampling of small (300 µl) oil samples for analysis was carried out from the engine while the engine was exploited. Fresh oil was used as a control sample. The induction of the oxidation was observed by the change in the intensity of the EPR signal with an increase in the mileage of the car.

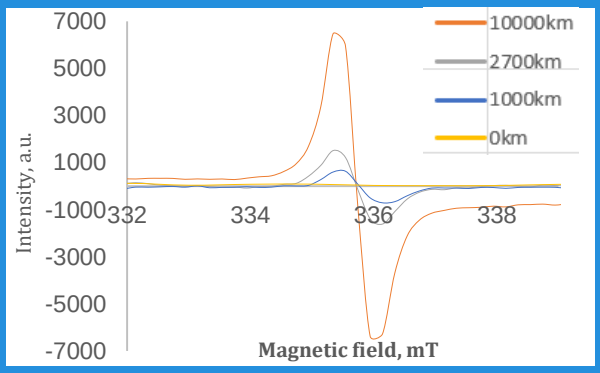
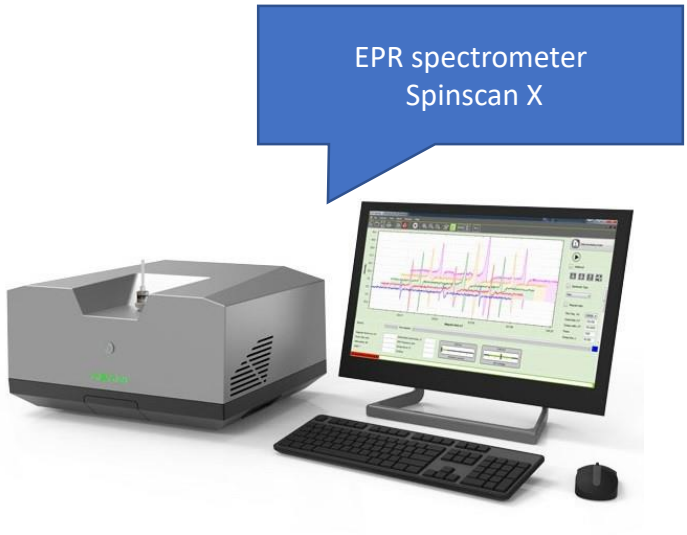


Figure 1. - Free radicals amplification in engine oil during engine operation.
Experiment parameters: Center field, 306.41 mT; Sweep width, 200 mT; Modulation frequency, 109.375 kHz; Modulation amplitude, 200 uT; Attenuation, 10 dB, Points 1000, Sweep time, 120 s.

The degradation of engine oil as a result of normal use in a gasoline engine by monitoring the content of free radicals was studied with using EPR spectrometer SPINSCAN X.

Free radicals in lubricating oils are formed as a result of their oxidation in internal combustion engines operating at high temperatures and speeds in the presence of oxygen. Therefore, they can be used as a marker of the age of the oil, as well as the potential stability and effectiveness of the lubricant. When the useful life of the oil nears its end, the signal intensity of organic free radicals increases dramatically. If not controlled, these radicals can lead to polymerization or separation of the molecules of the lubricant, resulting in poor lubricant performance.

Antioxidants are added to most synthetic motor oils, which react with any radicals formed, increasing the durability of oil. But even they are consumed during the operation of the car, and as a result, lubricating oil ceases to fulfill its intended purpose.



Numerous examples of EPR-based experimental research of oil and oil products and studies of petrochemical processes demonstrate the broad scope of practical applications of the EPR technique for gathering useful information about the quality of raw oil and oil products as well as about mechanisms of chemical processes occurring in oil at various conditions. The EPR spectroscopy can be used for deep scientific explorations as well as for finding new perspective ways of oil resources usage.