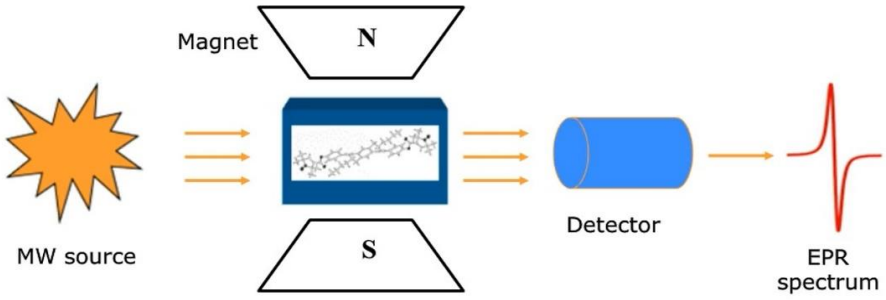
EPR-spectroscopy in photochemistry

The EPR technique is one of the most sensitive physical methods of detection, identification and study of free radicals, ion-radicals and triplet-state molecules generated during photochemical processes such as:

1) photodecomposition (homolytic photolysis into radicals, heterolytic photolysis into ions — photoionization);

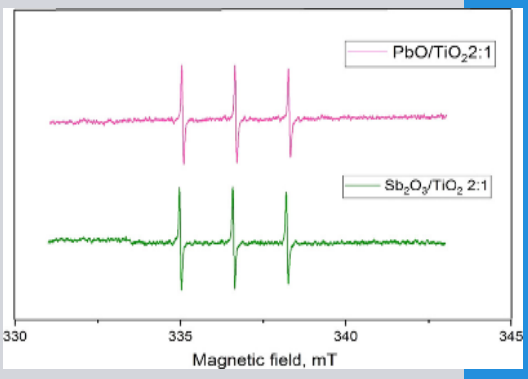
2) electron phototransfer (photooxidation, photoreduction, photodissotiative electron addition);

3) photosensibilization (photosensibilized oxidation, photosensibilized reduction,photosensibilized decay) [1].

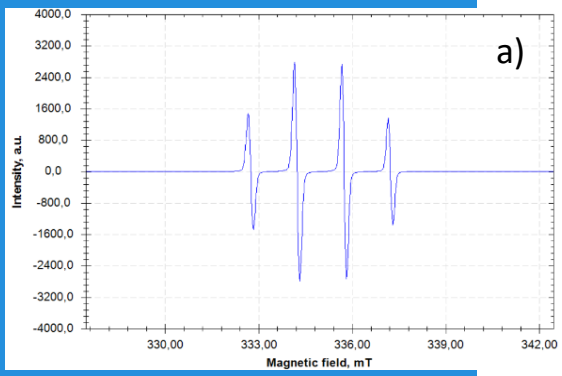


EPR spectroscopy was used to illustrate that degradation of organic Benzophenone-3 (BP-3) UV filter using Sb2O3/TiO2 and PBO/TiO2 photocatalysts under ultraviolet irradiation proceeds by a radical mechanism. The presence of a peak of the TEMP-1O2 adduct on the spectra indicates the participation of singlet oxygen in the degradation of the UV filter in sunscreen, which was detected in surface and groundwater [2].

Polymer materials for photovoltaics are subject to photodegradation, which occurs under the influence of UV radiation and leads to a decrease in conductive properties. Using the PS 100X EPR spectrometer and irradiation of the test sample with visible light directly in the resonator of the device in the temperature range 90-340K, the nature and environment of paramagnetic centers arising in a sample of a composite fullerene-containing polymer were studied [3].



EPR-based research [4] on CMS 8400 spectrometer showed, that the hydroxyl radical (·OH), generated during the photo-Fenton reaction mediated by hybrid materials catalyst α-Fe2O3-Graphene, is a major reaction product responsible for the rhodamine degradation – a model wastewaters pollutant.



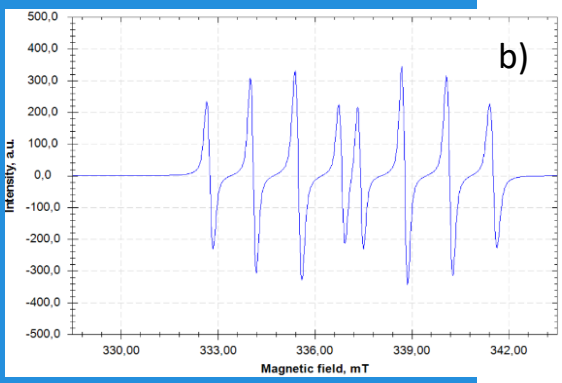


Figure 1 – EPR-spectra of UV-generated DMPO-OH (a) и DEPMPO-OH (b) radicals. Experiment parameters: center field 336.73mT; sweep width 12mT; modulation frequency 109.375kHz; modulation amplitude 200uT; attenuation 25dB; number of points 1000; sweep time 60s.

To demonstrate the application of EPR technique in photochemistry research the hydroxyl radicals UV-generation process has been used. The radicals have been detected on bench-top EPR spectrometer Spinscan X. Spin-trapping is the method for short-living radicals (such as the OH-radicals) detection. DMPO (3,4-dihydro-2,3-dimethyl-2H-pyrrole 1-oxide) и DEPMPO (P-(3,4-dihydro-2-methyl-1-oxido-2H-pyrrol-2-yl)-phosphonic acid, diethyl ester) solutions have been used as spin traps.

Hydroxyl radicals are generated in the reaction mixture consisting of 10mM H_2O_2 with 100mM DMPO or 50mM DEPMPO, under the UV irradiation with λ=395 nm. The DEUTERIUM TUNGSTEN HPOWER/LS-DWHP lamp was used as a UV-source, the light was directed onto the sample by using the optical fiber cable through the EPR-resonator window.

Numerous examples of EPR-based experimental research of photochemical processes demonstrate the broad scope of practical applications of the EPR technique for studying the irradiated products. The EPR spectroscopy can be used for deep scientific explorations in photochemistry and spin-photophysics as well as for the development of spin-based technologies, particularly: photolysis control, photonics and spintronics, - the frontier research areas allowing for new methods of photoinduced processes research.

Our solution –
EPR spectrometer
Spinscan X

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