

Photochemistry and EPR

● Gaining Insights with Light

Photochemistry plays an important role in many chemical processes. Irradiating a sample with a suitable wavelength of light often results in free radicals, radical pairs, excited states, or changes of oxidation state.

Electron Paramagnetic Resonance (EPR) is the best technique for gaining insight into these reactions and processes because of its unique ability to unambiguously detect paramagnetic species in a direct and non-intrusive manner.

EPR identifies the reaction intermediates as well as quantifies their concentrations, thus elucidating the reaction mechanisms and kinetics of photochemical reactions. It can be applied to samples in gaseous, liquid or solid states over a wide range of temperatures.

Challenge: Understanding photochemical reaction mechanisms as well as identification and quantitation of intermediate species that are often short-lived and extremely unstable.

Solution: The Bruker Magnettech ESR5000 benchtop EPR spectrometer package

- Monitors photochemical reactions for understanding of electron transfer mechanisms
- Identifies active intermediates, assesses their activity and provides mechanistic information
- Quantifies paramagnetic intermediates over the course of the reactions
- Measures the extent of degradation in polymers, food and beverages, pharmaceuticals, and many other products during light exposure

Health Care Product Stability

Photo-aging of Skin Care Products

Free radicals in skin care products are generated by UV exposure thereby damaging the skin via free radical reactions. Screening of a product's efficacy and safety can be evaluated via stress testing. There is a need for highly efficient antioxidants that are resistant to environmental oxidative stress and remain active over long time periods.

Evaluation of Antioxidants' Effect on a Skin Care Product During UV-irradiation:

The efficacy of antioxidants in skin care formulations depends on their penetration kinetics, reactivity with non-radical components, and photo-stability.

The Magnettech ESR5000 monitors the time-efficacy profile showing how fast an antioxidant can unfold its full potential in skin and how stable its activity is.

Photodegradation of Pharmaceutical Products

- Photodegradation of the drug Nifedipine after exposure to light shows the formation of nitrogen-based free radical. The amount of free radicals corresponds to the level of degradation.
- The time evolution of the free radicals is followed with EPR.
- The increasing amount of radicals shows the level of active pharmaceutical ingredient (API) degradation and can be used to predict product stability.

Magnettech ESR5000 Key Features:

- No prior EPR experience needed
- Accurate results
- Superior sensitivity
- Ease of use
- Full workflow for measuring, analyzing and quantifying impurities
- Compact foot print
- Low cost of ownership

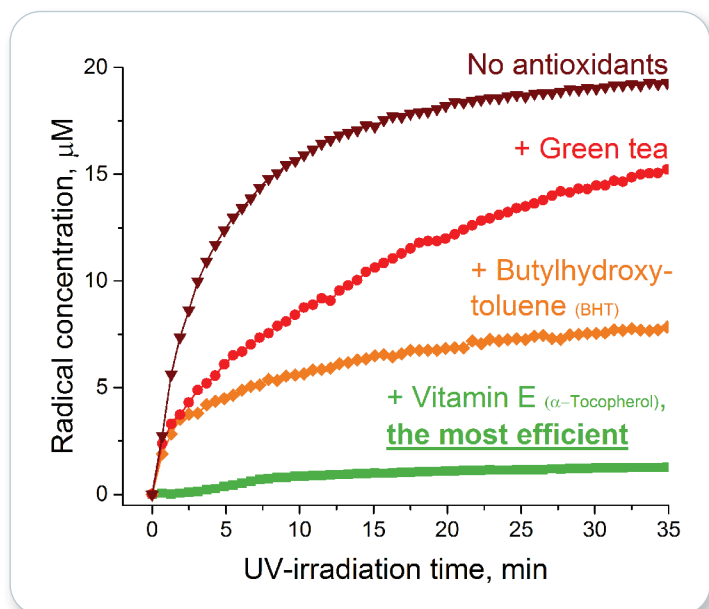


Figure 1. Effectiveness of antioxidants (green tea, BHT, and vitamin E) on skin care product aging upon UV-irradiation.

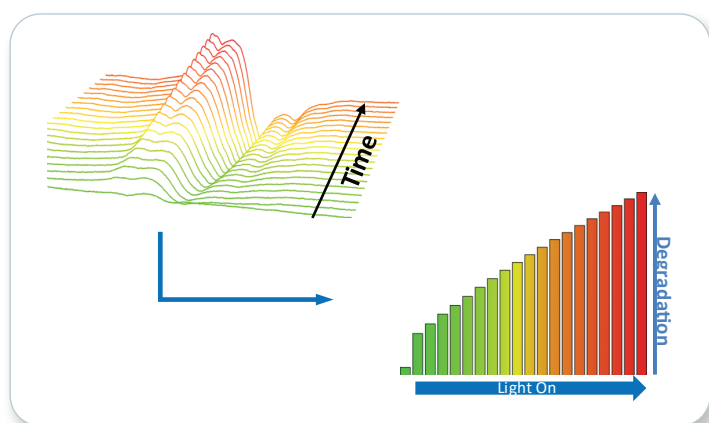


Figure 2. Photodegradation of Nifedipine - time evolution of N-based radical formed in the API.



Food and Beverage Quality

Beer Shelf Life

Flavor quality of beer is compromised by exposure to light resulting in photooxidation, a condition known as 'lightstruck'.

EPR sheds light on the reaction mechanism for the formation of this unpleasant flavor by detecting free radicals upon visible light exposure. Three radicals are identified and their reaction kinetics are monitored.

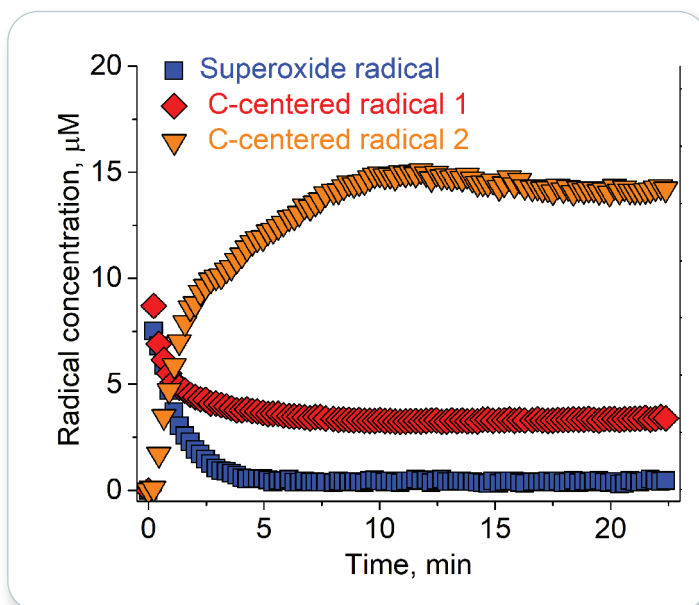


Figure 3. Radical formation in beer after UV-Vis irradiation. Spin trapping technique was used to capture the short lived radicals.

Edible Oil Photooxidation

- Photooxidation of unsaturated fatty acids results in rancidity of fat containing foods.
- Oxidation profiles and accurate free radical concentrations provide a measure for oxidative resistance at each stage of the production process.
- Stability of edible oils is enhanced by anti-oxidants. EPR enables manufacturers to make rapid and informed process control decisions to optimize product shelf life.

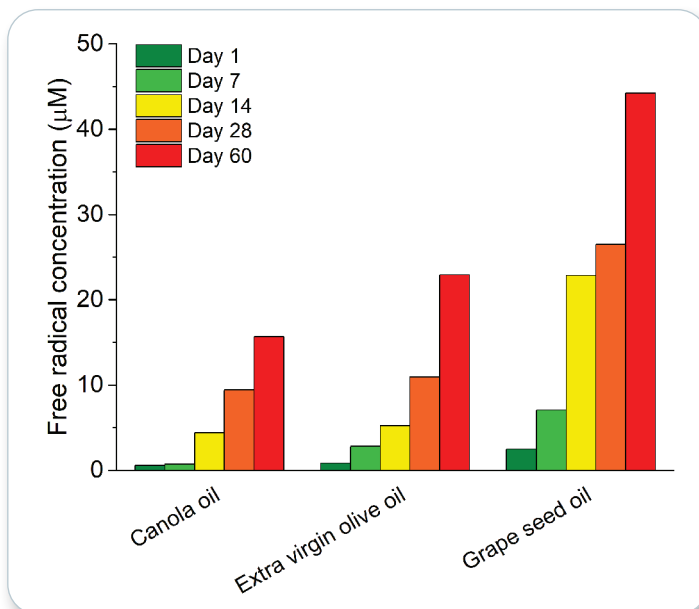


Figure 4. Quantitative radical analysis after window exposure of edible oils for 2 months.



Photostability of Materials

Protecting OLEDs

OLED (organic light-emitting diodes) aging often proceeds via breaking of weak bonds. This results in organic radicals that participate in unwanted secondary chemical processes. Charge-transfer reactions at electrode interfaces also involve organic radicals. Typical radical-

generating reagents are organic and inorganic lithium salts commonly used as interlayers between the cathode and the electron-transport layer (ETL). EPR detects and quantifies the radicals present in OLEDs.

Case study: Radical detection during charge-transfer reactions at the cathode interface

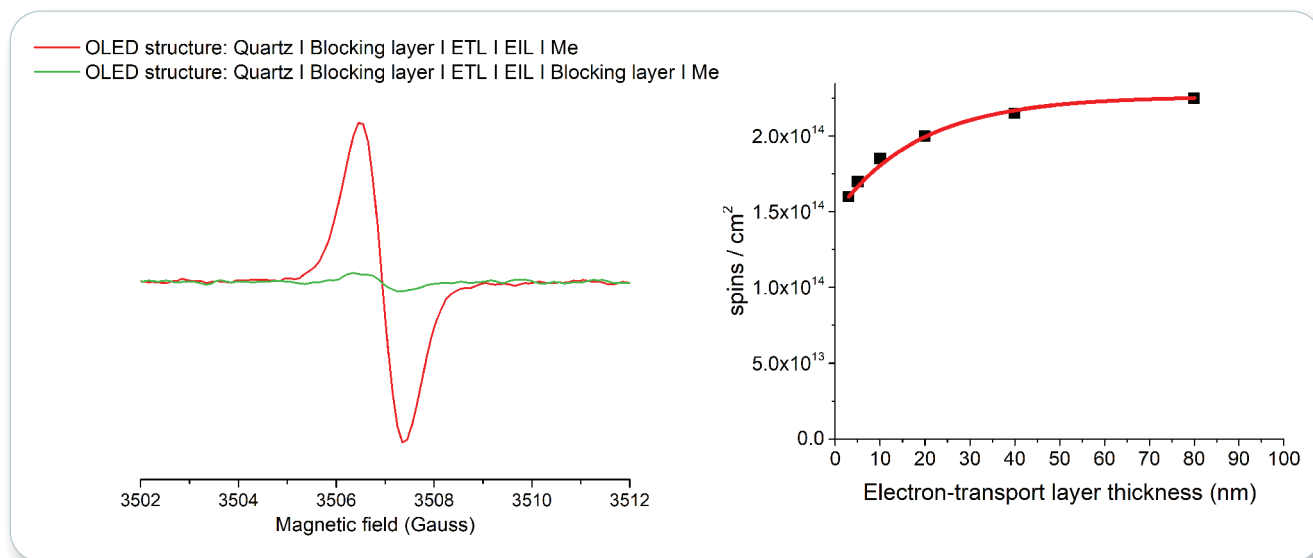


Figure 5A. EPR spectra of a sample of OLED structure with (green trace) and without (red trace) additional blocking layer.

Figure 5B. The area density of organic radicals as a function of electron-transport layer thickness.

- Having a blocking layer between the electron-injection layer (EIL) and the cathode metal (Me) greatly reduces the number of organic radicals (left panel). EPR results confirm that the second blocking layer reduces aging of OLEDs.
- Quantitative EPR analysis provides information about the density of organic radicals as a function of the ETL layer (right panel).



Photodegradation of Polymers

Radical reactions are involved in the various processes such as polymerization, cross-linking and degradation of polymers. It is possible to investigate these phenomena by using EPR spectroscopy in both academic and industrial settings for research and quality control.

The degradation of polymers due to light exposure leads to discoloration and a decrease in the mechanical properties (elasticity, toughness, etc). To prevent this decomposition, hindered amine light stabilizers (HALS) are added to the polymer. By monitoring the EPR signals of these light stabilizers, their effectiveness can be evaluated using the Magnettech ESR5000.

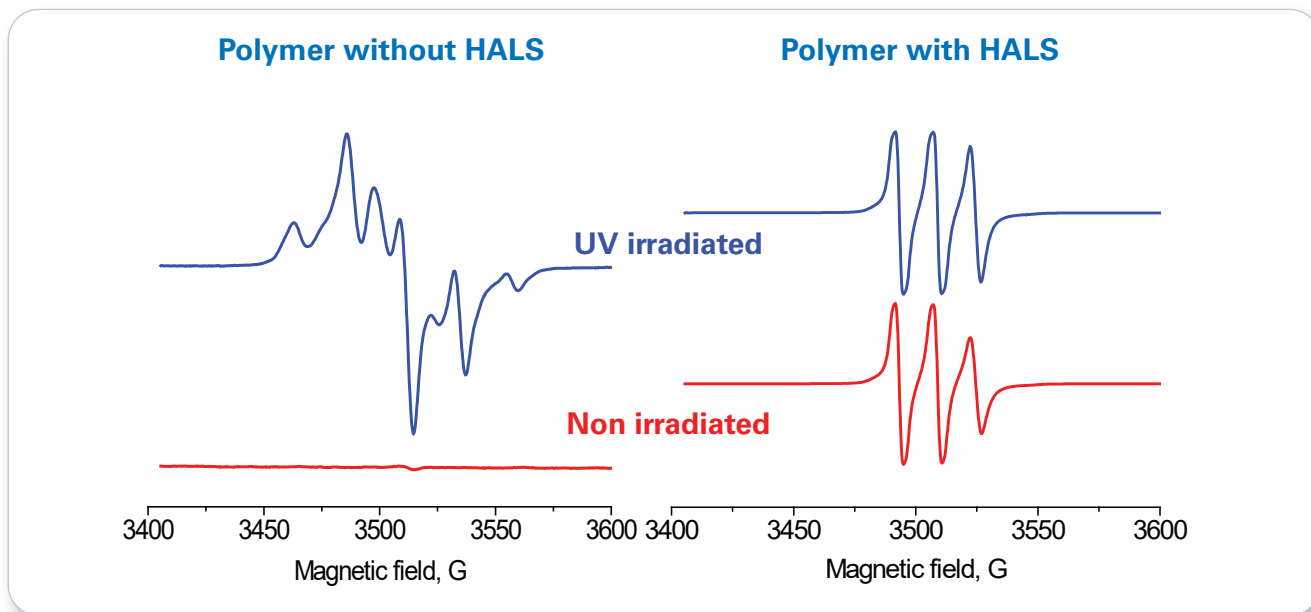


Figure 6A. EPR spectra of PolyMethyl-MethAcrylate (PMMA) without HALS before (red trace) and after (blue trace) UV-irradiation.

Figure 6B. EPR spectra of PolyMethyl-MethAcrylate (PMMA) with HALS before (red trace) and after (blue trace) UV-irradiation.

- The effectiveness of light stabilizers (HALS) for preventing polymer degradation by UV irradiation is easily evaluated with the Magnettech ESR5000.
- The EPR signal generated in the polymer during UV irradiation (left) is completely suppressed after addition of the HALS stabilizer where only the HALS EPR spectrum is observed (right panel).

- Magnettech ESR5000 detects HALS nitroxyl radicals generated during paint oxidation upon UV exposure.
- Quantitative EPR analysis shows correlation between the free radical concentration and the exposure duration confirming the effectiveness of HALS as an antioxidant

Case study : HALS EPR Signal indicating Deterioration after UV Exposure

The main cause of paint film deterioration is the degradation of several components, including the binder and pigments. This is caused by the formation of free radicals from prolonged exposure to UV light (sunlight), moisture and freeze-thaw cycles. Free radicals produced by UV are highly reactive and either build or break chemical bonds in substances. In the case of paint durability, on exposure to UV, the free radicals actually damage the film.

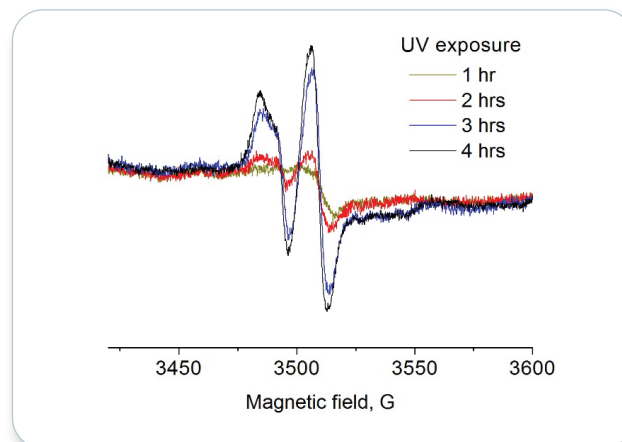


Figure 7. EPR spectra of detected free radicals after exposure of paint to sunlight. The time point are indicated in the figure legend.

Photodegradation of Paints

Case Study : EPR Study of Weathered Automotive Paint Systems using HALS

Long-term weathering performance of an automotive paint system is improved by antioxidants that prevent radical formation. The antioxidants must inhibit clearcoat photooxidation at the onset of exposure and sustain inhibition for many years. EPR based analytical techniques have been developed to estimate the longevity of HALS additives in clearcoat paint systems over long exposure times.

- The concentration of EPR-detected HALS radicals correlates to the amount of active HALS in automotive paint and quickly reaches a maximum during sun exposure at all locations.
- The rate at which active HALS is lost is very dependent on exposure location. This behavior qualitatively matches the sun load associated with these exposure locations: Belgium, 9 MJ/m²; Miami, Florida, 17 MJ/m² and, Townsville, Australia, 20 MJ/m².
- Quantitative EPR data suggest that while the paint system may be over stabilized for service in Belgium, it is under stabilized for service in high sun load environments.

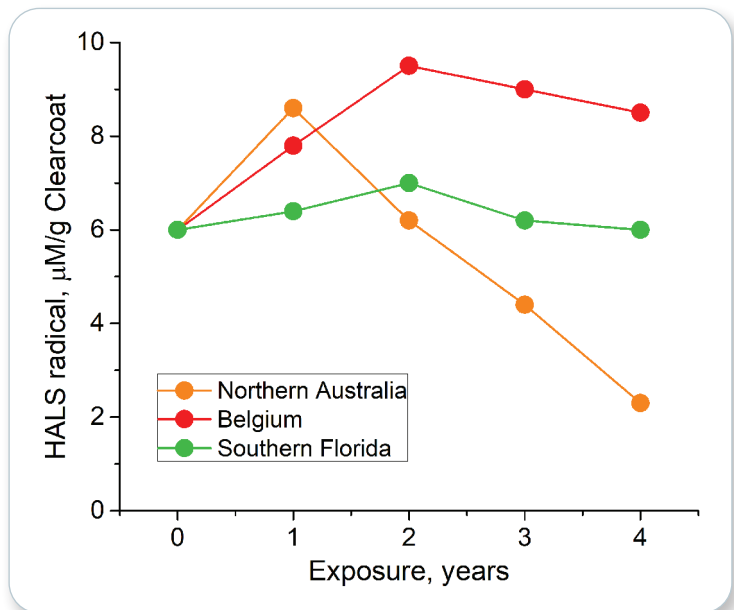


Figure 8. Quantitative EPR analysis of HALS radical formed in car paint after sunlight exposure at 3 different locations in Australia, Europe, and the US.



Photocatalysis

TiO₂ Photocatalysts

- Understanding of the photocatalytic mechanisms in TiO₂ photocatalysts is a prerequisite to improve their efficiency in a wide range of applications.
- EPR detects and identifies key active species (hydroxyl radical, superoxide, singlet oxygen) produced in irradiated TiO₂ suspensions
- Monitoring the radical intermediates by EPR using various wavelengths and solvents provides complete characterization of TiO₂ photo-activity

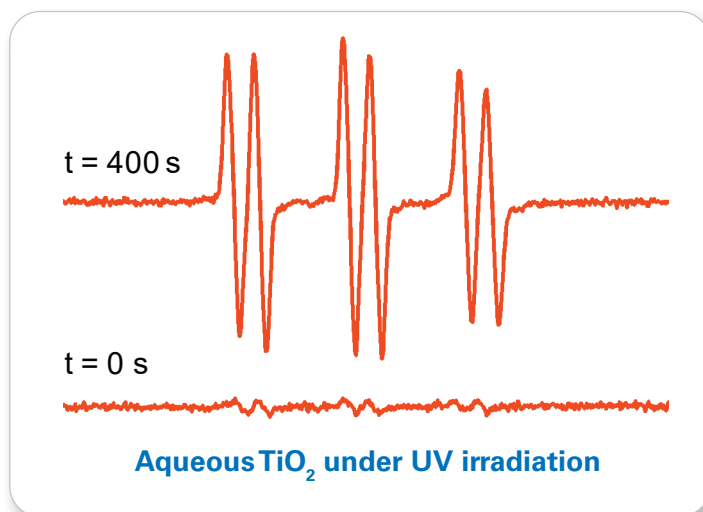
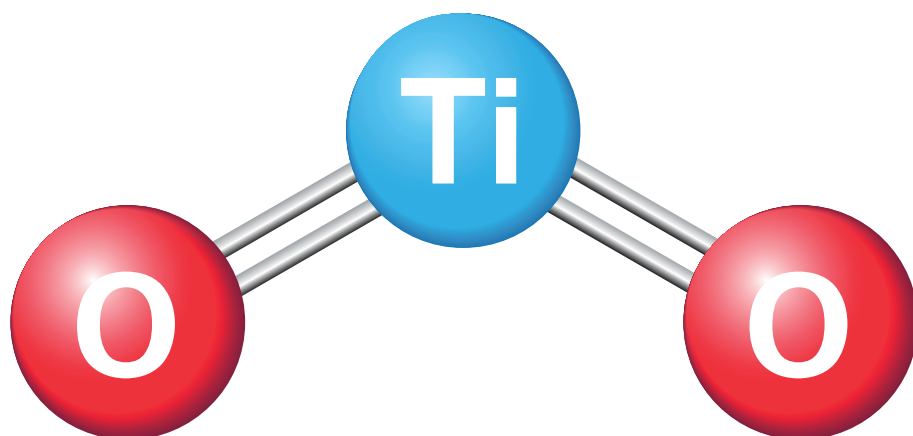
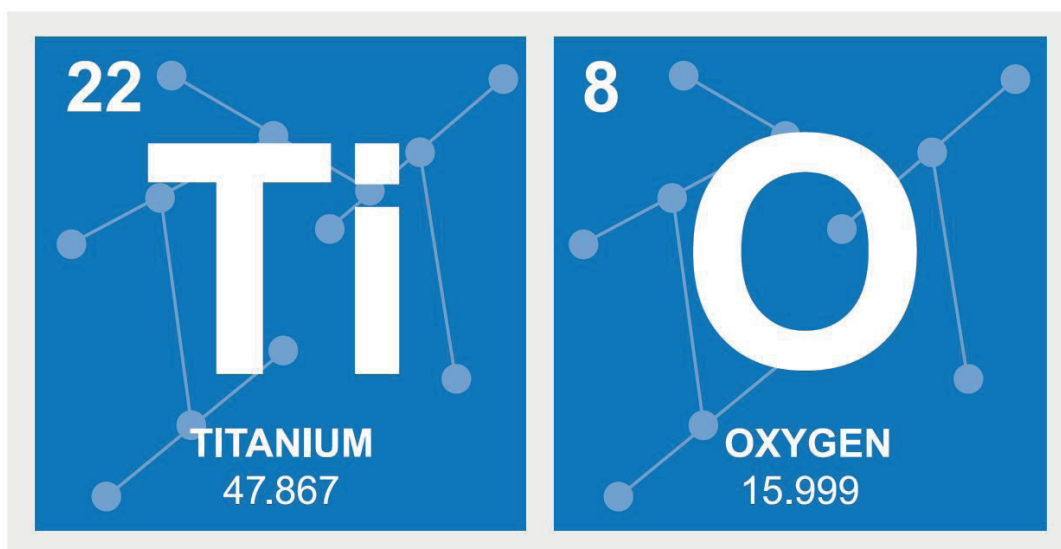
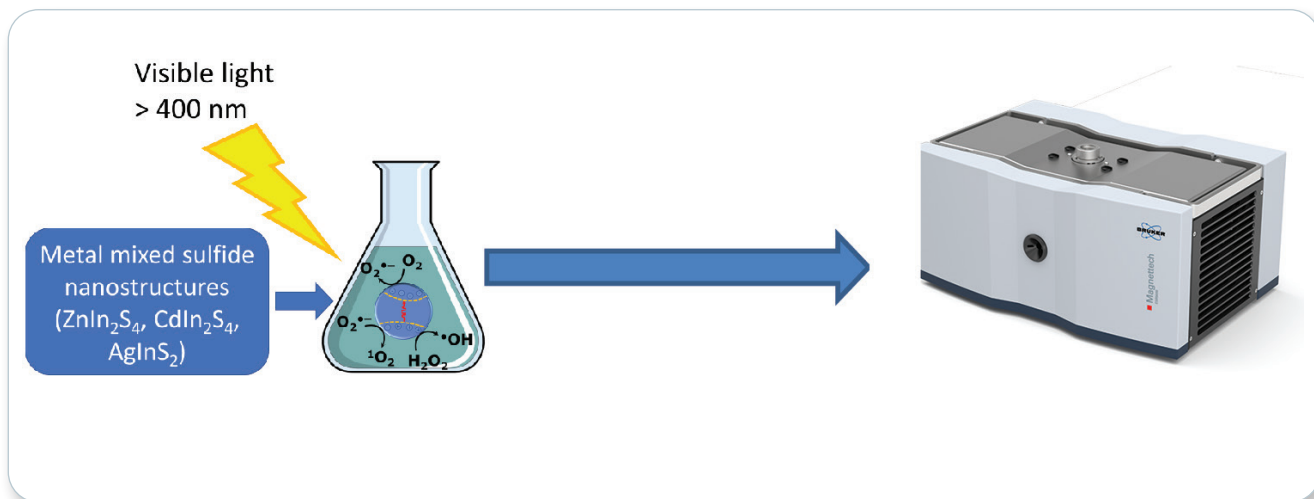


Figure 9. Free radical detection in UV-irradiated photocatalyst TiO₂. Spin trapping technique was used to capture the radicals.



Nanoparticles

- Photocatalytic nanomaterials (ZnIn_2S_4 , CdIn_2S_4 , AgInS_2) facilitate generation of reactive oxygen species (ROS) during irradiation with visible light.
- EPR detects and quantifies the formation of three different ROS – superoxide ($\text{O}_2^{\cdot-}$), hydroxyl radical ($\cdot\text{OH}$), and singlet oxygen ($^1\text{O}_2$).
- The photocatalytic and photobiological activity of the nanomaterials correlates with the ROS concentration monitored by EPR.
- The ability to promote ROS generation could be considered an intrinsic parameter of a given nanomaterial, similar to other physiochemical properties such as particle size, morphology, active surface area, etc.



Photopolymerization

- Photoinitiators are used to generate highly efficient radicals for the polymerization of methacrylates upon exposure to a blue light.
- The proposed mechanism states that the photoinitiation process proceeds via several radical species.
- Quantitative EPR analysis of all three intermediates (silyl, acyl, and phenyl radicals) provides information about the photopolymerization efficiency.

Summary:

Understanding photochemical reactions is crucial for many applications in science and technology. EPR provides the unique capability to directly measure the radicals that play a part in these reactions. By detecting, identifying, monitoring, and quantifying radical intermediates, the Magnetech ESR5000 sheds light on the underlying mechanisms.

The Magnetech ESR5000 UV-system features an integrated light source to safely irradiate both liquids and solids to observe radical intermediates and products. The broad irradiation spectrum offered by our UV light source can be selectively narrowed for specific applications with a variety of wavelengths. The exposure time can be easily controlled by ESRStudio software.

The ESRStudio software features a built in and easy to use quantification and identification package that enables a short time from data collection to full analysis.

With the host of available accessories and unique software capabilities the Magnetech ESR5000 benchtop solution can be easily tailored to an extensive range of applications.

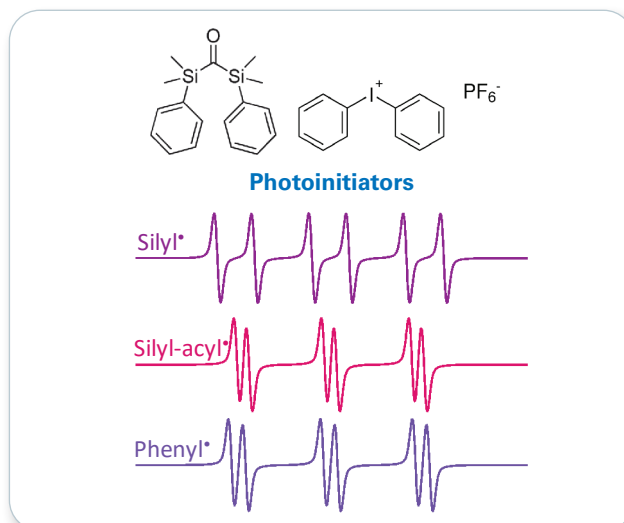


Figure 10. EPR spectra of radical species generated in photoinitiator bis-silylketone used for photopolymerization of methacrylates, e.g., in dental materials.

Further reading

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 - Gerlock J.L. (Ford Motor Company) et al., Determination of active HALS in automotive paint systems II: HALS distribution in weathered clearcoat/basecoat paint systems, *Polym. Degrad. Stab.* (2001) 73 201 *biol. Sci.* (2016) 15 1124
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