APPLICATION OF MICROWAVE-ASSISTED PHOTOCHEMISTRY

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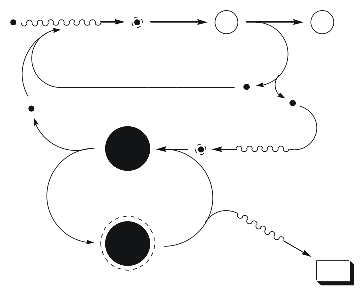
Photochemistry in the microwave field presents a combined chemical activation by two distinctive kinds of electromagnetic radiation. Energy of MW radiation (E = 0.4-40 J.mol^{-1} at ν = 1-100 GHz) is considerably lower than that of UV-VIS radiation (E = 600-170 kJ.mol^{-1} at λ = 200-700 nm) and is thus insufficient to disrupt bonds of common organic molecules.

Molecules with a permanent (or induced) dipole respond to an oscillating microwave field by rotating, which results in friction with neighboring molecules and thereby in heat. On the other hand, the UV-VIS radiation can bring about electronic excitation of molecules and trigger their photochemical transformation.

The objective of photochemistry in the MW field is often connected to the electrodeless discharge lamp (EDL), which generates UV-VIS radiation when placed into the MW field (see figure).

The principle of EDL operation:



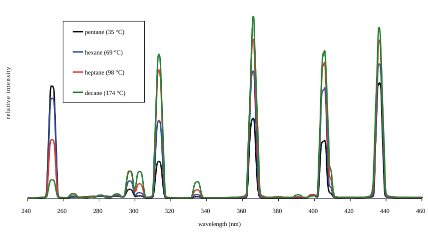
The spectral output of electrodeless discharge lamps depends on numerous factors such as temperature of the ambient environment, EDL envelope material, solvent used in a photochemical reaction, amount of the filling substance, and the intensity and the nature of the MW field.

Knowledge of EDL spectral characteristics is essential for planning of photochemical experiments. The right selection of the fill material and the proper setting of experimental conditions can provide a desired UV-VIS radiation.

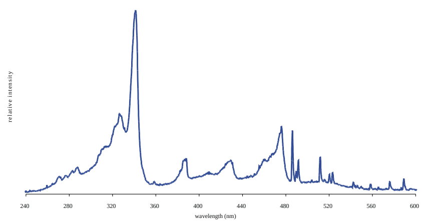
The MW-photochemical reactor containing EDL allows simultaneous irradiation of the sample by both MW and UV/VIS radiation, which might be of use in numerous environmental applications (MW-assisted photochemical oxidation employed in waste-water treatment; MW-assisted photochemical degradation of organic and inorganic pollutants - see similarities between the solar spectrum and the spectrum of sulfur EDL).

Spectral characteristics of several EDLs and the solar spectrum:

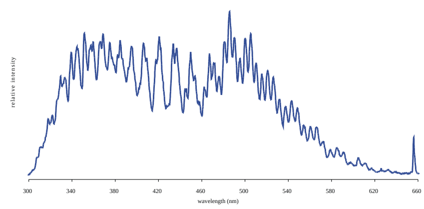
Quartz Hg-EDL in several n-alkanes (different b.p.)



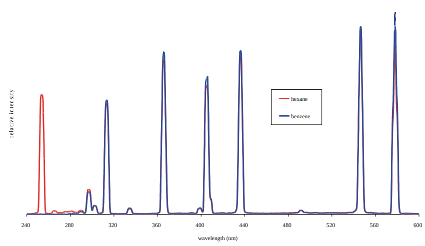
Quartz I-EDL in n-decane (b.p. 174 °C)



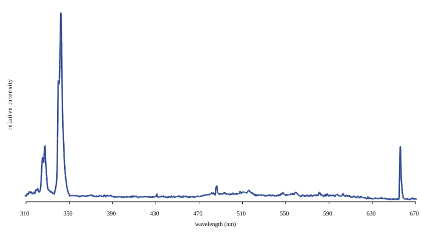
Pyrex S-EDL in n-decane (b.p. 174 °C)



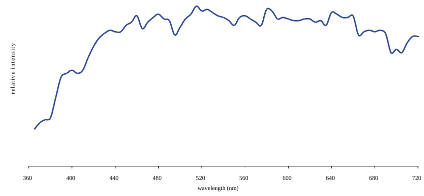
Hg-EDL in UV-transparent and non-transparent solvents



Pyrex P-EDL in n-decane (b.p. 174 °C)



Sunlight spectrum



- *Simultaneous UV and MW irradiation.*
- *"Wireless" EDL operation (convenient for high-pressure experiments).*
- *Low cost of EDL, simple use.*
- *Variability of spectral output (change of fill or experimental conditions).*
- *High photochemical efficiencies.*
- *Use of inexpensive domestic MW oven.*

- *Impaired stability of some EDLs at higher temperatures (overheating).*
- *Technical difficulties to carry out experiments at temperatures below the solvent boiling point.*
- *Polar solvents lower the output efficiency of EDL.*
- *Higher safety precautions.*

References:

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