Chemical Actinometry
IUPAC Technical Report

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Introduction

Chemical actinometer or dosimeter: chemical system (fluid, gas, solid or in a microheterogeneous environment) that undergoes a light-induced reaction (at a certain wavelength, λ) for which the quantum yield, **$\Phi(\lambda)$, is accurately known**. Measuring the reaction rate allows the calculation of the absorbed photon flux.

The incident **photon flux (amount basis)** $q^0_{n,p}(\lambda)$ is calculated from the amount of photons absorbed: $q_{n,p}(\lambda) = q^0_{n,p}(\lambda)[1-10^{-A(\lambda)}]$ provided that the **linear decadic absorbance *A*(λ)** is constant ± 10 % during the irradiation time. Should this not be the case, integration of the differential absorbance over time would be necessary.

The most convenient situation is for total absorption during the whole irradiation period, i.e., $q_{n,p}(\lambda) = q^0_{n,p}(\lambda)$

Determination of conversion to the products (see Scheme) affords the total number of photons absorbed by the liquid or gas volume or solid surface which may have any form or geometry.

The **quantum yield** of a photochemical reaction is defined as $\Phi(\lambda)$ = the number of events, e.g., molecules changed, formed or destroyed, divided by the number of absorbed photons of that particular wavelength in the same period of time, i.e.,

$$\Phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

Differentially:

$$\Phi(\lambda) = \frac{\mathrm{d}x/\mathrm{d}t}{q^0_{n,p}(\lambda)[1-10^{-A(\lambda)}]}$$

d*x*/d*t* : rate of change of a measurable quantity (spectral or any other property).

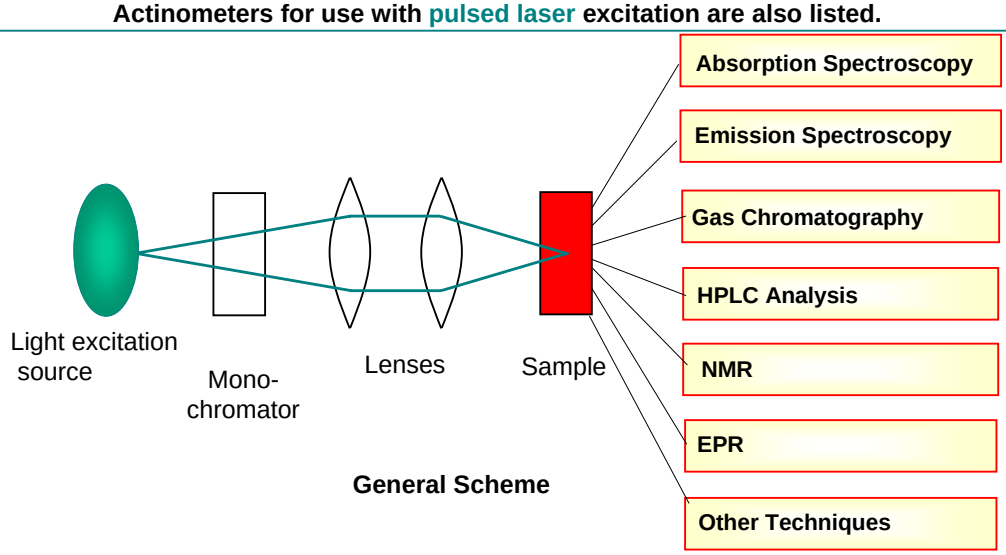
Strictly, the term quantum yield applies only for monochromatic excitation.

Calibration of the actinometer is done by applying a calibration lamp or by absolute measurement of incident photon flux (using, e.g., a calibrated radiometer, a calorimeter, or a photodiode).

Photothermal methods[1] are often used to calibrate actinometers.

Project Objective

Produce a complete list of systems and recommended procedures for the determination of the reaction quantum yield, Φ, in solid, gas, and liquid samples upon excitation with λ = 200-900 nm
Conditions for selection of actinometers are throughly discussed.
The actinometers are organized by phase and by wavelength within each phase.
Actinometers for use with pulsed laser excitation are also listed.



General Scheme

1. **"Quantities, Terminology, and Symbols in Photothermal and Related Spectroscopies "**, IUPAC Recommendations 2004, M. Terazima, N. Hirota, S.E. Braslavsky, A. Mandelis, S.E. Bialkowski, G.J. Diebold, R.J.D. Miller, D. Fournier, R.A. Palmer, A. Tam, Physical and Biophysical Chemistry Division, *Pure Appl. Chem. 76*, 1083-1118 (2004)]