

The Chemical Sections on Actinometry **Rumin Wang***

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Editorial

The Photochemistry Commission and subsequently the Subcommittee on Photochemistry decided to update and expand the document. In particular, the sections on gas-phase and solid-state actinometers have been expanded. The terms associated with radiation quantities are made according to the world organization for Standardization (ISO) recommendations, and an inventory of terms used is included. Some actinometers are added, whereas others are deleted from the list with recommended procedures for his or her use. The latter has been due to various reasons. In some cases, the actinometer reagent is no longer commercially available, and in other cases, the complexity of the procedure for the use or disposal of the waste does not justify the inclusion of the actinometer during a recommended list. According to the "Glossary of terms utilized in photochemistry", an actinometer may be a chemical system or a physical device by which the amount of photons during a beam absorbed into the defined space of a apparatus are often determined integrally or per time.

A chemical actinometer or dosimeter is a chemical system (fluid, gas, solid, or in a micro heterogeneous 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 q_p is calculated from the relation $q_p(\text{abs}, \lambda) = q_p o(\lambda) (1 - 10^{-A(\lambda)})$, as long as the decade absorbance $A(\lambda)$ is constant ± 10 that in the irradiation time. Should this not be the case, integration of the differential absorbance over time would be necessary. The easiest case is for $q_p(\text{abs}, \lambda) = q_o(\lambda)$ for total absorption during the entire irradiation period. Determination of conversion to the products affords the entire number of photons absorbed by the liquid or gas volume or solid surface, which can have any form or geometry. The quantum yield of a photochemical reaction is defined as $\Phi(\lambda) = \frac{\text{number of events}}{\text{number of photons absorbed}}$. Calibration of an actinometer is done by applying a calibration lamp or by absolute measurement of irradiance (CA), photochemical conversion is directly related to the number of photons absorbed because the chemical action of light means reversible or irreversible chemical process, i.e., destruction or buildup of molecules and, consequently, of their properties like spectra. Chemical actinometry has been employed for about 70 years in photochemistry as a comparatively simple and accurate method for radiation measurement. Owing to the recent progress in the development of radiation detectors, semiconductors, and

Department of Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

*Corresponding author:

Rumin Wang

✉ wangmin19@mail.nwpu.edu.cn

Tel: +8615109297930

Department of Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

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electronic equipment, physical devices furnished with a direct readout become more and more popular among photo chemists for the measurement of radiation.

Physical devices are often preferred to CAs for the case of straightforward irradiation geometries due to their easy, fast, and precise performance. However, these outstanding properties are inherent in just a little number of electrically calibrated radiometers (ECRs) available during a few highly equipped laboratories. ECRs are special thermopiles or piezoelectric radiometers, which may be calibrated in an absolute manner by electrical substitution without the necessity of any standard. The majority of physical detectors, like usual thermopiles, piezoelectric joule meters, or photodiodes are only secondary standards, the response of which may be subject to changes. The sensitivity of a joule meter may decrease with use thanks to surface damage by high-power radiation. The same is valid for thermopiles. The spectral sensitivity of the widespread silicon photodiodes is even altered without use, just by aging. The extent of this effect depends on the wavelength home in which the detector are going to be used. An 18 and reduce in sensitivity at 300 nm in one year was reported to be a typical value. Visually unnoticeable damage of photodiodes occurs during exposure

to high irradiation levels (generally quite 10 mW cm^{-2} for silicon photodiodes in continuous wave experiments) leading to an irreversible decrease of sensitivity and severe inhomogeneities within the surface.

Consequently, occasional recalibration of radiation detectors

against a typical is strongly recommended. In contrast to the physical detectors, well-established CAs led to accurate absolute radiation measurements, provided that they are employed according to the recommended procedures. These CAs are proven reproducible and don't demand any recalibration.