Fotokataliza - Slovar izrazov

Photocatalysis - Glossary of terms

Photokatalyse - Glossar der Begriffe

Photocatalyse - Glossaire de termes

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Photocatalysis - Glossary of terms

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Contents

Page

European foreword

This document (CEN/TS 16981:2016) has been prepared by Technical Committee CEN/TC 386 "Photocatalyse", the secretariat of which is held by AFNOR.

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Introduction

Photocatalysis is a very efficient advanced oxidation technique which enables the production of active species following light absorption by the photocatalyst, such as bound/free hydroxyl radicals (·OH), perhydroxyl radicals (·OOH), conduction band electrons and valence band holes, capable of partly or completely mineralising/oxidising the majority of organic compounds. The most commonly used photocatalyst is titanium dioxide (TiO_2), the latter being thermodynamically stable, non-toxic and economical. It can be used in powder form or deposited on a substrate (glass fibre, fabrics, plates/sheets, etc.). The objective is to introduce performance standards for photo-induced effects (including photocatalysis). These standards will mainly concern test and analysis methods.

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1 Scope

A common language for standards, disclosed to a wide audience and referring only to the operational protocols and to their outcomes, is needed both for a consistent set of standards and the connection with the scientific literature. This glossary will take into account existing glossary of terms used in *photocatalysis* and *photochemistry*. Because in *photocatalysis* numerous properties are difficult to be evaluated, it is strongly recommended in standard norms to avoid reporting properties depending on number of actives sites, the mechanisms of adsorption or kinetic mechanisms of photocatalytic reactions. For the same reason instead of the *quantum yield* and related quantities it is easier to report the *photonic efficiency*.

Most of the definitions reported in this Technical Specification are a sub-set of the IUPAC definitions in *photocatalysis* and radiocatalysis [1]. Some other definitions, in particular for the *photocatalytic rate* and reactors are taken from a dedicated work [2]. The use and many technical specifications on the physical values suggested for irradiation conditions in the standards are reported in a separate Technical Specification [3].

The arrangement of entries is alphabetical, and the criterion adopted by the IUPAC has been followed for the typeface used: *italicized words* in a definition or following it indicate a cross-reference in the Glossary.

2 Generalities

2.1 Note on units

SI units are adopted, with some exceptions, prominently in the use of the *molar decadic absorption coefficient*, ε, with common units $dm^3 \, mol^{-1} \, cm^{-1}$ and a mole of photons denoted as an *einstein*. Note that "amount concentration" is the preferred term for what has been known as "molar concentration", and is complementary to the terms "mass concentration" and "number concentration".

2.2 Note on symbols

Functional dependence of a physical quantity f on a variable x is indicated by placing the variable in parentheses following the symbol for the function; e.g., $\varepsilon(\lambda)$. Differentiation of a physical quantity f with respect to a variable x is indicated by a subscript x; e.g., the typical *spectral radiant power* quantity $P_\lambda = dP/d\lambda$. The natural logarithm is indicated with *ln*, and the logarithm to base 10 with *log*.

For the magnitudes implying energy or photons incident on a surface from all directions, the set of symbols recommended by the International Organization for Standardization (ISO) [4] and included in the IUPAC "Green Book", and by the International Commission on Illumination [5] are adopted, i.e., H_o or F_o for *fluence*, E_o for *fluence rate*, $H_{p,o}$ or $F_{p,o}$ for *photon fluence*, and $E_{p,o}$ for *photon fluence rate*, note the letter o as subscript. This has been done primarily to comply with internationally agreed-upon symbols. It is important, however, to avoid confusion with the terms used to designate an amount of energy (or photons) prior to *absorption*. In these cases, the superscript 0 (zero) is used.

2.3 Note on the relationship between spectral, radiometric, and photonic quantities

When a quantity expressed in photonic units (G_p) covers a *wavelength* range (polychromatic irradiation between λ_1 and λ_2), then G_p is the integral between λ_1 and λ_2 of the corresponding spectral photonic quantity, $G_p(\lambda)$:

$$G_p = \int_{\lambda 1}^{\lambda 2} G_p(\lambda) \, d\lambda \text{ (e.g., } spectral \ photon \ flux\text{).}$$

CEN/TS 16981:2016 (E)

Since a spectral radiometric or energetic quantity at a given *wavelength* λ ($G_{e,\lambda}$, e.g., *spectral radiant power*, $P_{\lambda/W}$ nm^{-1}, is related to the corresponding photonic quantity at the same *wavelength* ($G_{p,\lambda}$, e.g., *spectral photon flux* / s^{-1} nm^{-1}) by the relation:

$$G_{e,\lambda} = E(\lambda)\, G_{p,\lambda}$$

with

$E(\lambda) = h\,c/\lambda$, the energy of a *photon* of *wavelength* λ.

The relation between photonic (G_p) and corresponding radiometric (or energetic, G_e) quantity is given by:

$$G_e = h\,c \int_{\lambda 1}^{\lambda 2} G_p(\lambda)\, 1/\lambda\, d\lambda$$

or, more useful in practice:

$$G_p = (1/h\,c) \int_{\lambda 1}^{\lambda 2} G_e(\lambda)\lambda\, d\lambda$$

Therefore, for example, to calculate a *photon flux* over a *wavelength* interval, the *spectral distribution* of the *radiant power* is necessary. Note that in the Glossary no sub-index e has been used for the radiometric quantities. Radiometric quantities (G_e, as above, *radiant power* and others) are needed because *lamp* providers usually give the *spectral distribution* of the *lamps* in these units, and not in photonic units (G_p, *photon flux* and other photonic quantities) and because of quantification of radiation using, e.g., radiometers.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
absorbance, A_e
logarithm to the base 10 (linear *absorbance*) of the incident (prior to *absorption*) *spectral radiant power,* P_λ^0 divided by the transmitted *spectral radiant power*, P_λ:

$$A(\lambda) = \log\left(\frac{P_\lambda^0}{P_\lambda}\right) = -\log T(\lambda)$$

Note 1 to entry: $T(\lambda)$ is the (internal) *transmittance* at the defined *wavelength*. The terms absorbancy, *extinction*, and *optical density* should no longer be used. When natural logarithms are used, the napierian *absorbance* is the logarithm to the base e of the incident *spectral radiant power*, P_λ^0 divided by the transmitted *spectral radiant power*, P_λ:

$$A_e(\lambda) = \ln\left(\frac{P_\lambda^0}{P_\lambda}\right) = -\ln T(\lambda)$$

Note 2 to entry: These definitions suppose that all the incident *ultraviolet*, *visible*, or *infrared* radiation is either transmitted or absorbed, reflection or scattering being negligible. *Attenuance* should be used when this supposition cannot be made.

Note 3 to entry: In practice, A is the logarithm to the base 10 of the *spectral radiant power* of *ultraviolet*, *visible*, or *infrared* radiation transmitted through a reference sample divided by that transmitted through the investigated sample, both observed in identical cells.

Note 4 to entry: In common usage, A is given for a path length of 1 cm, unless otherwise specified.

Note 5 to entry: Traditionally, (spectral) *radiant intensity*, I_λ, was used instead of *spectral radiant power*, P_λ, now the accepted term.

Note 6 to entry: The *wavelength* symbol as a subscript for *P* and in parenthesis for *T* and *A* may be omitted. However, the *wavelength* should be specified for which the value of the particular property is reported.

Note 7 to entry: Same as internal *optical density*, which is a term not recommended.

Note 8 to entry: *See also absorption coefficient, absorptance, attenuance, Beer–Lambert law, Lambert law, molar absorption coefficient.*

3.2
absorbed (spectral) photon flux density

number of photons of a particular *wavelength*, per time interval (*spectral photon flux*, number basis, $q_{p,\lambda}$, or *spectral photon flux*, amount basis, $q_{n,p,\lambda}$) absorbed by a system per volume, *V*

Note 1 to entry: On number basis, SI unit is s^{-1} m^{-4}; common unit is s^{-1} cm^{-3} nm^{-1}. On amount basis, SI unit is mol s^{-1} m^{-4}; common unit is *einstein* s^{-1} cm^{-3} nm^{-1}

Note 2 to entry: Mathematical expression: $\dfrac{q_{p,\lambda}^0\left[1-10^{-A(\lambda)}\right]}{V}$ on number basis, $\dfrac{q_{n,p,\lambda}^0\left[1-10^{-A(\lambda)}\right]}{V}$ on amount basis, where $A(\lambda)$ is the *absorbance* at *wavelength* λ and superscript 0 (zero) indicates incident photons.

Note 3 to entry: Absorbed (spectral) *photon flux* density (number basis or amount basis) is used in the denominator when calculating a differential *quantum yield* and using in the numerator the rate of change of the number, dC/dt, or the rate of change of the amount concentration, dc/dt, respectively.

3.3
absorbed (spectral) radiant power density

spectral radiant energy per time interval (*spectral radiant power*, P_λ) absorbed by a system per volume, *V*

Note 1 to entry: SI unit is W m^{-4}; common unit is W cm^{-3} nm^{-1}.

Note 2 to entry: Mathematical expression: $\dfrac{P_\lambda^0\left[1-10^{-A(\lambda)}\right]}{V}$ where $A(\lambda)$ is the *absorbance* at *wavelength* λ and superscript 0 (zero) indicates incident *radiant power*.

3.4
absorptance, *a*

fraction of *ultraviolet*, *visible*, or *infrared* radiation absorbed, equal to one minus the *transmittance* (*T*), i.e., (1 - *T*)

Note 1 to entry: The use of this obsolete term, equivalent to *absorption factor*, is not recommended.

Note 2 to entry: See also *absorbance*.

3.5
absorption (of electromagnetic radiation)
transfer of energy from an electromagnetic field to a material or a molecular entity

Note 1 to entry: In a semiclassical fashion, this transfer of energy can be described as being due to an interaction of the electric field of the wave with an oscillating electric dipole moment set up in the material or molecular entity. This dipole moment is the result of the perturbation by the outside field, and its oscillation *frequency ν* is given by the difference *ΔE* of the energies of the lower and upper state in the absorbing material or molecular entity, *ΔE = hν*. When the *frequency* of the oscillating dipole moment and the *frequency* of the field agree, a resonance occurs and energy can flow from the field into the material or molecule (an *absorption* occurs).

Note 2 to entry: When energy flows from the material or molecule to the field, stimulated light *emission* occurs.

Note 3 to entry: The oscillating electric dipole moment produced in the material or molecular entity has an amplitude and direction determined by a vector M_{if}, known as the electric transition (dipole) moment. The amplitude of this moment is the transition moment between the initial (i) and final states (f).

3.6
absorption coefficient (linear decadic *a* or linear napierian *α*)
absorbance, *A(λ)*, divided by the optical pathlength, *l*:

$$a(\lambda) = \frac{A(\lambda)}{l} = \left(\frac{1}{l}\right)\log\left(\frac{P_\lambda^0}{P_\lambda}\right)$$

where

P_λ^0 and P_λ are, respectively, the incident and transmitted *spectral radiant power*. When napierian logarithms are used

$$\alpha(\lambda) = a(\lambda)\ln 10 = \left(\frac{1}{l}\right)\ln\left(\frac{P_\lambda^0}{P_\lambda}\right)$$

where

α   is the linear napierian *absorption coefficient*.

Note 1 to entry: Since *absorbance* is a dimensionless quantity, the coherent SI unit for *a* and α is m^{-1}; the common unit is cm^{-1}.

Note 2 to entry: See also *absorptivity*, *molar absorption coefficient*.

3.7
absorption cross-section, *σ*
linear napierian *absorption coefficient*, *α(λ)*, divided by the number of molecular entities contained in a volume of the absorbing medium along the *ultraviolet*, *visible*, or *infrared* radiation path:

$$\sigma(\lambda) = \frac{a(\lambda)}{C} = \frac{1}{Cl}\ln\left(\frac{P_\lambda^0}{P_\lambda}\right)$$

where

C is the number concentration of molecular entities (number per volume), l is the optical pathlength, and P_λ^0 and P_λ are, respectively, the incident and transmitted *spectral radiant power*.

Note 1 to entry: SI unit is m^2, common unit is cm^2.

Note 2 to entry: The relation between the *absorption cross-section* and the *molar* (*decadic*) *absorption coefficient,* $\varepsilon(\lambda)$, is $\alpha(\lambda)$ = ln10 $\varepsilon(\lambda)/N_A$ with N_A the Avogadro constant. A conversion equation in common units is:

$$\sigma(\lambda)/\text{cm}^2 = (3.8236 \times 10^{-21}/\text{mol}) \times [\varepsilon(\lambda)/ \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}].$$

Note 3 to entry: See also *attenuance*, *Beer–Lambert law*.

3.8
absorption factor

fraction of *ultraviolet*, *visible*, or *infrared* radiation absorbed by a system

$$f(\lambda) = 1 - T(\lambda) = 1 - 10^{-A(\lambda)}$$

with

$T(\lambda)$ the *transmittance* and $A(\lambda)$ the *absorbance* at a particular *wavelength* λ.

Note 1 to entry: This term is preferred to *absorptance*.

Note 2 to entry: The *wavelength* symbol may be omitted for *f*, *T*, and *A*. The *wavelength* should be specified for which the value of the particular property is reported.

Note 3 to entry: For $A(\lambda)$ << 1/ln10, $f(\lambda) \approx A(\lambda)$ ln10.

3.9
absorption spectrum

plot of the *absorbance* or of the *absorption coefficient* against a quantity related to *photon* energy, such as *frequency v*, *wavenumber* $\tilde{v}$, or *wavelength* λ

3.10
absorptivity

absorptance divided by the optical pathlength

Note 1 to entry: The unit length shall be specified.

Note 2 to entry: The use of this obsolete term is not recommended.

Note 3 to entry: For very low *attenuance*, i.e., for $A(\lambda)$ << 1/ln10, it approximates the linear *absorption coefficient*, within the approximation $[1 - 10^{-A(\lambda)}] \approx A(\lambda)$ ln10.

3.11
actinic

applied or referred to *actinism. R*elating to, resulting from, or exhibiting chemical changes produced by radiant energy especially in the *visible* and *ultraviolet* parts of the spectrum

3.12
actinism

chemical changes on living and nonliving materials caused by optical radiation

CEN/TS 16981:2016 (E)

3.13
actinometer

chemical system for the determination of the number of *photons* integrally or per time interval absorbed into the defined space of a chemical reactor

Note 1 to entry: This name is commonly applied to systems used in the *ultraviolet* and *visible wavelength* ranges.

Note 2 to entry: For example, solutions of potassium oxalatoferrate(III), $K_3[Fe(C_2O_4)_3]$ (among other systems) can be used as a chemical *actinometer*. Bolometers, thermopiles, and photodiodes are physical devices giving a reading of the radiation impinging on them that can be correlated to the number of photons detected as well as to the number of photons entering the chemical reactor.

Note 3 to entry: *See also spectral sensitivity.*

3.14
action spectrum

plot of a relative biological or chemical photoresponse (=Δy) per number of incident (prior to *absorption*) *photons*, vs. *wavelength*, or energy of radiation, or *frequency* or *wavenumber*

Note 1 to entry: This form of presentation is frequently used in the studies of biological or solid-state systems, where the nature of the absorbing species is unknown.

Note 2 to entry: It is advisable to ensure that the *fluence* dependence of the photoresponse is the same (e.g., linear) for all the *wavelength*s studied.

Note 3 to entry: The *action spectrum* is sometimes called *spectral respon*sivity or sensitivity spectrum. The precise *action spectrum* is a plot of the spectral (*photon* or quantum) effectiveness. By contrast, a plot of the biological or chemical change or response per absorbed *photon* (quantum efficiency) vs. *wavelength* is the *efficiency spectrum*.

Note 4 to entry: In cases where the *fluence* dependence of the photoresponse is not linear (as is often the case in biological photoresponses), a plot of the photoresponse vs. *fluence* should be made at several *wavelength*s and a standard response should be chosen. A plot of the inverse of the "standard response" level vs. *wavelength* is then the *action spectrum* of the photoresponse.

Note 5 to entry: See also *excitation spectrum*, *efficiency spectrum*.

3.15
AM 0 sunlight

solar *irradiance* in space just above the atmosphere of the earth on a plane perpendicular to the direction of the sun (air mass, AM, zero)

Note 1 to entry: Also called extraterrestrial *irradiance.*

Note 2 to entry: See also *AM 1 sunlight.*

3.16
AM 1 sunlight

solar *irradiance* at sea level, i.e., traversing the atmosphere, when the direction of the sun is perpendicular to the surface of the earth

Note 1 to entry: Also called terrestrial global *irradiance.*

Note 2 to entry: See also *AM 0 sunlight.*

3.17
amalgam *lamp*

see *mercury lamp*

3.18
attenuance, *D*

logarithm to the base 10 of the incident *spectral radiant power*, P_λ^0, divided by the transmitted *spectral radiant power*, P_λ

$$D(\lambda) = \log\left(\frac{P_\lambda^0}{P_\lambda}\right) = -\log T(\lambda)$$

where

T(λ)   is the *transmittance*

Note 1 to entry: *Attenuance* reduces to *absorbance* if the incident beam is only either transmitted or absorbed, but not reflected or scattered.

Note 2 to entry: See also *Beer–Lambert law*, *depth of penetration*.

3.19
attenuance filter
(better use: *neutral-density filter*)

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3.20
back electron-transfer

term often used to indicate thermal inversion of *excited-state electron transfer* restoring the donor and acceptor in their original oxidation state

Note 1 to entry: Process better designated as *electron back-transfer*.

Note 2 to entry: In using this term, one should also specify the resulting electronic state of the donor and acceptor.

Note 3 to entry: It is recommended to use this term only for the process restoring the original electronic state of donor and acceptor.

Note 4 to entry: Should the forward *electron transfer* lead to *charge separation*, *electron back-transfer* will result in *charge recombination*.

3.21
bandgap energy, E_g

energy difference between the bottom of the *conduction band* and the top of the *valence band* in a semiconductor or an insulator

Note 1 to entry: See also *Fermi level.*

3.22
bandpass filter

optical device that permits the transmission of radiation within a specified *wavelength* range and does not permit transmission of radiation at higher or lower *wavelength*s

CEN/TS 16981:2016 (E)

Note 1 to entry: It can be an interference or a colored *filter*.

Note 2 to entry: See also *filter*.

3.23
bathochromic shift (effect)
shift of a spectral band to lower *frequency* (longer *wavelengths*) owing to the in*fluence* of substitution or a change in environment (e.g., solvent)

Note 1 to entry: It is informally referred to as a *red shift* and is opposite to a *hypsochromic shift.*

3.24
Beer–Lambert law (or Beer–Lambert–Bouguer law)
the *absorbance* of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the *absorption* pathlength, *l*, and to the concentration, *c*, or (in the gas phase) to the pressure of the absorbing species

Note 1 to entry: This law holds only under the limitations of the *Lambert law* and for absorbing species exhibiting no concentration or pressure dependent aggregation. The law can be expressed as

$$A(\lambda) = \log\left(\frac{P_\lambda^0}{P_\lambda} \right) = \varepsilon(\lambda) cl$$

or

$$P_\lambda = P_\lambda^0\, 10^{-A(\lambda)} = P_\lambda^0\, 10^{-\varepsilon(\lambda) cl}$$

where the proportionality constant, $\varepsilon(\lambda)$, is the molar (decadic) *absorption coefficient*, and P_λ^0 and P_λ are, respectively, the incident and transmitted *spectral radiant powers*. For *l* in cm and *c* in mol dm^{-3} (M), $\varepsilon(\lambda)$ will result in dm^3 mol^{-1} cm^{-1} (M^{-1} cm^{-1}), a commonly used unit. SI unit of $\varepsilon(\lambda)$ is m^2 mol^{-1} (10 dm^3 mol^{-1} cm^{-1}).

Note 2 to entry: *Spectral radiant power* shall be used because the *Beer–Lambert law* holds only if the spectral bandwidth of the *ultraviolet*, *visible*, or *infrared* radiation is narrow as compared to spectral linewidths in the spectrum.

Note 3 to entry: See also *absorbance, attenuance, extinction coefficient, Lambert law*.

3.25
bioluminescence
luminescence produced by living systems

Note 1 to entry: See also *luminescence.*

3.26
biphotonic excitation
simultaneous (*coherent*) *absorption* of two *photons* (either same or different *wavelength*), the energy of excitation being the sum of the energies of the two photons

Note 1 to entry: Also called *two-photon excitation*.

Note 2 to entry: This term is sometimes also used for a two-step *absorption* when the *absorption* is no longer simultaneous.

3.27
biphotonic process
resulting from *biphotonic excitation*

Note 1 to entry: See also *multiphoton process*.

3.28
bleaching
in *photochemistry*, this term refers to the loss of *absorption* or *emission intensity*

3.29
blue shift
informal expression for *hypsochromic shift*

3.30
Brewster angle, θ_B
when an unpolarized planar electromagnetic wavefront impinges on a flat dielectric surface, there is a unique angle (θ_B), commonly referred to as *Brewster angle*, at which the reflected waves are all polarized into a single plane

Note 1 to entry: Expression for *Brewster angle*: θ_B = arctan (n_2 / n_1) = arctan (ε_2 / ε_1)$^{1/2}$ where n_2 and n_1 are the refractive indices of the receiving surface and the initial medium, respectively, and ε_2 and ε_1 are the relative static permittivities (formerly called *dielectric constant*s).

Note 2 to entry: For a randomly polarized beam incident at *Brewster angle*, the electric fields of the reflected and refracted waves are perpendicular to each other.

Note 3 to entry: For a wave incident from air on water (n = 1,333), glass (n = 1,515), and diamond (n = 2,417), the *Brewster angle*s are 53, 57, and 67,5 degrees, respectively.

3.31
charge hopping
electron or hole transport between equivalent sites

3.32
charge recombination
reverse of *charge separation*

Note 1 to entry: In using this term, it is important to specify the resulting electronic state of the donor and acceptor.

3.33
charge separation
process in which, under a suitable in*fluence* (e.g., *photoexcitation*), electronic charge moves in a way that increases (or decreases) the difference in local charges between donor and acceptor sites

Note 1 to entry: *Charge recombination* reduces (or increases) the difference.

Note 2 to entry: *Electron transfer* between neutral species is the most common example of *charge separation*. The most important example of *charge recombination* is electron backtransfer occurring after photoinduced *charge separation*.