INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

DIVISION OF ORGANIC AND BIOMOLECULAR CHEMISTRY
SUB-COMMITTEE ON PHOTOCHEMISTRY*

Chemical Actinometry

(IUPAC Technical Report)

Prepared for publication by

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Abbreviations:

AM = analytical method

CA = chemical actinometer

E = electronic device

G = gas phase

GC= gas chromatography

HPLC = high pressure liquid chromatography

IR = infra-red

L = liquid phase

LC = liquid chromatography

PP = procedure, precautions, comments

S = solid phase

WR = wavelength range

SYMBOLS AND UNITS USED IN THIS DOCUMENT

Common units are mentioned if different from SI base units

Name	Definition	Symbol	Unit	
			SI base[a]	**common**
absorbance (in general)	$A = \log(P^0/P) = -\log T$	A_λ	---[b]	
at a particular wavelength λ	$A_\lambda = \log(P_\lambda^0/P_\lambda) = -\log T_\lambda$	A	---[b]	
absorption coefficient (decadic)	$a_\lambda = A_\lambda/l = (1/l)\log(P_\lambda^0/P_\lambda)$	a	cm^{-1}	
absorption cross section	$\sigma_\lambda = (\varepsilon_\lambda/N_A)\ln 10 = 3.8236 \times 10^{-21}\ \varepsilon_\lambda$, with N_A Avogadro constant and ε_λ in mol^{-1} dm^3 cm^{-1}	σ	cm^2	
actinometric factor, see Sensitivity				
concentration		c	mol dm^{-3} = M	
fluence [c]		H'	J m^{-2}	
frequency (linear)		ν	Hz	
irradiance, [c] *radiant power* per unit area, incident from all directions. For a parallel and perpendicularly incident beam not scattered or reflected by the target or its surroundings *fluence rate* (E') is an equivalent term.	$E = dP/dS$ (with S the area)	E	W m^{-2}	
lifetime, the time needed for the concentration of an entity to decrease to 1/e of its original value		τ	s	
molar (decadic) absorption coefficient	$\varepsilon_\lambda = A_\lambda/(c\, l)$	ε_λ	m^2 mol^{-1}	dm^3 mol^{-1} cm^{-1} = M^{-1} cm^{-1}
mole of photons			mol	einstein
optical pathlength		l	cm	
photon flux [c,d] number of photons per unit time	$N_p = dQ_p/dt$	N_p or q_p	s^{-1} or mol s^{-1} [e]	einstein s^{-1} [e]
photon fluence [c] number of photons per unit area	$H'_p = dQ_p/dS$	H'_p	m^{-2} or mol m^{-2} [e]	einstein m^{-2} [e]
photon fluence rate [c] applied to radiation falling from all directions	$E'_p = d H'_p/dS$	E'_p	m^{-2} s^{-1} or mol m^{-2} s^{-1} [e]	einstein m^{-2} s^{-1} [e]
photon irradiance [c] photon flux incident on a surface, identical to photon fluence rate for a parallel beam not scattered or reflected	$E_p = dN_p/dS$	E_p	m^{-2} s^{-1} or mol m^{-2} s^{-1} [e]	einstein m^{-2} s^{-1} [e]
photon number		Q_p	1	
pressure		p	Pa	
quantum yield	$\Phi = \dfrac{\text{number of events}}{\text{number of photons absorbed}}$	Φ	---[b]	
quantum yield of charge carrier formation in a photodiode	Φ_c			

Name	Definition	Symbol	Unit	
radiant energy		Q	J	
radiant exposure [c]		H	J m^{-2}	
radiant intensity [c]	$I = \mathrm{d}P / \mathrm{d}\Omega$	I	W sr^{-1}	
radiant power, radiant energy per unit time	$P = \mathrm{d}Q / \mathrm{d}t$	P	W	
radiative lifetime, the *lifetime* of an excited molecular entity in the absence of *radiationless transitions*.	$\tau_0 = 1/k_r$ with k_r the rate constant of the radiative step or the sum of rate constants for the radiative steps should there be more than one.	τ_0	s	
sensitivity of an actinometer	$S = \Phi_\lambda \Delta\varepsilon_\lambda$, with $\Delta\varepsilon_\lambda$ the variation in the molar absorption coefficient at the observation wavelength	S	m^2 mol^{-1}	dm^3 mol^{-1} cm^{-1}
sensitivity of a photodiode, photocurrent per watt of incident radiation		$S_{\lambda,w}$	A W^{-1}	
temperature		θ	K	°C
time		t	s	h
transmittance	$T = P_\lambda/P_\lambda^0$	T	--- [b]	
wavelength		λ	m	
wavenumber	in vacuum $\tilde{\nu} = \nu/c_0$ in a medium $\sigma = 1/\lambda$	$\tilde{\nu}, \sigma$	m^{-1}	

[a] accepted prefixes may be used to signify decimal multiples and submultiples of SI basic units.

[b] Dimensionless quantity.

[c] This quantity can be defined at *wavelength λ* per unit wavelength interval, in which case it is called the spectral quantity and carries the subindex λ

[d] In photochemistry Φ is reserved for quantum yield.

[e] If amount of photons is used.

The names, units and symbols have been mainly taken from the ISO Handbook on Quantities and Units, Part 6: Light and related electromagnetic radiations, ISO 31-6:1992(E).

The unit of concentration (c) most commonly used is mol dm^{-3} (M) and we have used it in this collection. According to IUPAC the symbol M should not be used with prefixes signifying multiples or submultiples, rather powers of 10 should be used. The optical pathlengths (l) are usually in cm. Consequently, the unit derived for the decadic molar absorption coefficient (ε) used in this collection is dm^3 mol^{-1} cm^{-1}.

Preface

The first version of this list appeared in *Pure Appl. Chem.* **61** (1989) 187-210. Since then, some methods have been improved, and some procedures have been modified. The Photochemistry Commission (1998-2001) and subsequently the Sub-Committee on Photochemistry (from 2001) decided to update and expand the document. In particular, the sections on gas-phase and solid state actinometers have been expanded. The terms related to radiation quantities have been made consistent with the International Organization for Standardization (ISO) recommendations, and a list of terms used is included. Some actinometers have been added whereas others have been deleted from the list with recommended procedures for their 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 for the disposal of the waste does not justify the inclusion of the actinometer in a recommended list.

According to the "Glossary of Terms Used in Photochemistry" (IUPAC Recommendations 1996), an actinometer is a chemical system or a physical device by which the number of photons in a beam absorbed <u>into</u> the defined space of a chemical reactor can be determined integrally or per unit time [1].

A **chemical actinometer** or dosimeter is a 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, Φ_λ, is accurately known. Measuring the reaction rate allows the calculation of the absorbed photon flux (the incident photon flux is calculated from the relation $N_{\mathrm{abs},\lambda} = N_{0,\lambda} (1 - 10^{-A\lambda})$, provided that the absorbance A_λ is constant $\pm 10\,\%$ during the irradiation time. Should this not be the case, integration of the differential absorbance over time would be necessary. The easiest case is for $N_{\mathrm{abs},\lambda} = N_{0,\lambda}$ for total absorption during the whole irradiation period. Determination of conversion to the products 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.

Calibration of an actinometer is done by applying a calibration lamp or by absolute measurement of irradiance (using, *e.g.*, a calibrated radiometer, a calorimeter, or a photodiode). Photothermal methods are often used to calibrate actinometers in absolute terms.

Absolute measurement of incident irradiance (E in W m^{-2}) or photon irradiance (E_p in quanta s^{-1} m^{-2} or einstein s^{-1} m^{-2}) or photon flux, N_p (einstein s^{-1}) using precalibrated photodiodes is described in section II.3. of this document.

For details and references concerning radiometry and actinometry, principles of photochemistry, light sources, and reactors, as well as possible sources of error when performing actinometric measurements, read **Section I** of this document and consult, *e.g.*,

Braun, A.M., Maurette, M.-T., Oliveros, E. *Photochemical Technology*, John Wiley & Sons, 1991, ISBN 0 471 92652 3; *idem, Technologie Photochimique,* Presses Polytechniques Romandes, Lausanne, 1986; *CRC Handbook of Organic Photochemistry* (Scaiano, J.C., ed.), 2 Vols., CRC Press, Boca Raton 1989;

Murov, S.L., Carmichael, I., Hug, G.L. *Handbook of Photochemistry*, Marcel Dekker, 2nd Edition, New York 1993.

For the most recent version of *Glossary of Terms and Definitions Used in Photochemistry* refer to:

Verhoeven, J.W. *Pure & Appl. Chem.* **68** (1996) 2223-2286; available at http://www.unibas.ch/epa/ . A new version is under preparation.

I. General Considerations on Chemical Actinometry

I.1. Pros and cons of chemical actinometry

In a chemical actinometer (CA) photochemical conversion is directly related to the number of photons absorbed because the chemical action of light means reversible or irreversible chemical change, *i.e.*, destruction or buildup of molecules and, consequently, of their properties such as spectra. Chemical actinometry has been employed in photochemistry as a relatively simple and accurate method for radiation measurement since about 70 years [2].

Due to the recent progress in the development of radiation detectors, semiconductors and electronic equipment, physical devices furnished with a direct readout become more and more popular among photochemists for the measurement of radiation. Physical devices are often preferred to CAs for the case of simple irradiation geometries because of their easy, fast, and precise performance.

However, these outstanding properties are inherent in only a small number of electrically calibrated radiometers (ECRs) available in a few highly equipped laboratories. ECRs are special thermopiles [3] or piezoelectric radiometers [4,5], which can be calibrated in an absolute manner by electrical substitution without the need of any standard. The majority of physical detectors, like usual thermopiles, piezoelectric joulemeters or photodiodes are only secondary standards, the response of which can be subject to changes.

The sensitivity of a joulemeter may decrease with use due to surface damage by high power radiation. The same is valid for thermopiles. The spectral sensitivity of the widespread silicium photodiodes is even altered without use, just by aging. The extent of this effect depends on the wavelength range in which the detector will be used. An 18 % decrease in sensitivity at 300 nm in one year was reported to be a typical value [6]. Visually unnoticeable damage of photodiodes occurs during exposure to high irradiation levels (generally more than 10 mW cm^{-2} for silicon photodiodes in continuous wave experiments) resulting in an irreversible decrease of sensitivity and severe inhomogeneities in the surface. Consequently, occasional recalibration of radiation detectors against a standard is strongly recommended.

In contrast to the physical detectors, well established CAs lead to accurate absolute radiation measurements, provided that they are employed according to the recommended procedures. These CAs have been proven reproducible and do not demand any recalibration.

I.2. Quality marks of a chemical actinometer

An established CA should meet the following requirements:

The photochemical system should be simple and well studied. The photoreaction must be reproducible under well-defined and easily controllable experimental conditions. Quantum yields should be accurately known for a large number of wavelengths. A wide usable spectral range and wavelength-independent quantum yields are desired.

The chemical components should be thermally stable to exclude complications due to dark reactions.

The analytical methods should be simple. Direct spectrophotometric analysis is preferred.

The system should display large sensitivity.

The handling of the photochemical system and the evaluation of the number of photons absorbed should be simple and straightforward.

The actinometric material should be easy to synthesize and purify. Preferably it should be commercially available. Disposal of the waste should be straightforward.

The CAs offered in the present list meet the requirements mentioned above in various degrees. Each system suffers also from disadvantages and a careful selection among the CAs is appropriate, depending on the intended experiment. **It is highly recommended to read the original literature on each actinometer prior to its use**.

I.3. Fields of application of chemical actinometry

It is important to mention that chemical actinometry covers only the wavelength range up to 795 nm.

In photochemical experiments involving a complex irradiation geometry (*e.g.*, photoreactors of the merry-go-round type) CAs serve best for the purpose of absolute radiation measurement and are unrivalled by physical devices. In any case, in photobiological and photochemical laboratories with less sophisticated equipment but where workers are experienced in chemical techniques, chemical actinometry is the standard procedure for radiation measurement.

Photochemists using physical equipment for radiation measurements need standards for the occasional recalibration of their detectors. CAs are the first choice for this procedure. For detectors with wavelength-independent response like thermopiles and joulemeters, the calibration by CAs is particularly easy since calibration at only one wavelength is sufficient.

Measurements of laser pulse energies can conveniently be done by joulemeters. At high laser powers most CAs will probably lose accuracy and sensitivity due to multiple photon processes occurring at high photon densities. However, if linearity of the joulemeter readout is guaranteed, a periodically repeated calibration by CAs at reduced laser power is an easy way of controlling the accuracy of the power meter. Those CAs which have been investigated especially at high photon fluxes using laser excitation can be used as standards for this purpose [7].

I.4. Potential errors in chemical actinometry

The detailed description of the chemical system, the limitations and the possible sources of errors for each CA should be made explicit in every publication. In the following only general aspects are discussed.

I.4.1. Refractive index

In this paragraph the discussion will be restricted to the case of monochromatic irradiation. Only in this case, a CA yields the radiant power P entering the sample cell, since a CA yields a photon rate or flux N_p (photons or einstein s^{-1}) entering the sample cell at a given wavelength. In the case of polychromatic irradiation conversion of photon flux to radiant power needs not only the knowledge of quantum yields and absorbances of the CA in the wavelength range considered, but also the spectral distribution of the irradiation source.

A correction for the reflectance R should be performed in order to obtain the radiant power of the irradiation beam P_B, *i.e.*, $P_B = P/(1 - R)$, or the photon flux of the irradiation beam $N_{p,0} = N_p/(1 - R)$.

Assuming that the incident radiation strikes the sample surface at a right angle, the reflectance at the boundary between two materials of refractive indices n_1 and n_2 can be calculated through the Fresnel law:

$$R = \left[\frac{n_1 - n_2}{n_1 + n_2} \right]^2$$

While entering a quartz sample cell the radiation passes the boundaries air/quartz and quartz/solution suffering reflections at each boundary. R is approximately the sum of the reflection losses at both boundaries whereby the second contribution is smaller than the first. Consequently, only the wavelength dependence of the refractive index of quartz determines the wavelength dependence of R. At 250 nm (1 - R) amounts to 0.955 for 2,2,2-trifluoroethanol ($n = 1.29$), to 0.959 for toluene ($n = 1.49$), and to 0.956 for CS_2 ($n = 1.63$). At 400 nm and 800 nm these values are higher by 0.005 and

0.007, respectively.

Thus, a mean value of $1 - R = 0.96$ can be applied for the calculation of P_B or of $N_{p,0}$ by introducing an additional error of 0.5 % at most. From the above estimation it follows that when comparing a photochemical system with a CA in different solvents an error of at most 0.4 % will be introduced should the correction be omitted. Deviations from this estimation are negligible for non-polarized as well as polarized radiation as long as the angle of the incident radiation with respect to the plane of the sample lies between 70 and 90 degrees [8].

I.4.2. Temperature

The influence of temperature variation has been investigated only for a small number of CAs. Temperature may influence an actinometric system through the temperature dependency of the quantum yield, the density of solvents, and possible competing dark reactions.

Photochemical quantum yields usually do not depend on temperature or only do so slightly. The temperature-induced changes in density lead to a corresponding change in concentration and consequently to an apparent change in chemical conversion. This effect can easily be cancelled out by measuring the conversion at the temperature of CA calibration or by calculation using tabulated density values. However, in some cases a large temperature variation of the possible dark reactions may take place. Therefore, actinometric measurements at temperatures different from the recommended range should be avoided.

I.4.3. Absorption by photoproducts

Ideally, in the wavelength range of a particular CA photoproducts should not absorb. In this case a high dynamic range of the actinometric measurement (number of photons, photon flux) can be expected. If photoproducts do absorb an inner filter will develop, this leading to a reduced conversion range. This difficulty should be considered with great care and extrapolation of the data to infinitely low conversion is recommended.

I.4.4. Degree of absorption by the CA

Some CAs are designed for incomplete absorption of the actinic light. This arrangement is particularly advantageous for the case of high photon flux, since the irradiated volume can be large, thus avoiding inhomogeneity problems during photoreaction. Since in this case additional errors are introduced by light reflections and the necessary measurements of transmission during irradiation, these systems are unfavourable for the measurement of low levels of radiation.

CAs exhibiting complete absorption of the radiation allow convenient measurement and easy evaluation and are thus preferred. At high absorbance the penetration depth of irradiation is small. Therefore, at the high photon flux met *e.g.*, in laser beams, severe inhomogeneity problems arise, which cannot be overcome even by effective stirring. This possible source of error is insufficiently discussed in the literature. Since at high absorbances the photoreaction occurs only in a very small reaction volume multiple photonic processes can be expected at high photon flux as often reported [7].

I.4.5. Polychromatic quantum counters

CAs with wavelength-independent quantum yields allow polychromatic quantum counting in the specified wavelength range provided complete absorption is maintained. In this case, each photon entering the actinometric solution causes chemical conversion with the same probability regardless of its energy. Polychromatic quantum counters are

particularly accurate due to their wavelength-independent conversion yield.

References to section I.

1. Verhoeven, J.W. *Pure & Appl. Chem*. **68** (1996) 2223-2286.

2. Leighton, W.G., Forbes, G.S. *J. Am. Chem. Soc*. **52** (1930) 3139-3152.

3. Bischoff, K. *Optik* **28** (1968/69) 183-189.

4. Phelan, Jr. R.J., Cook, A.R. *Applied Optics* **12** (1973) 2494-2500.

5. Geist, J., Blevin, W.R. *Applied Optics* **12** (1973) 2532-2535.

6. Gardner, J.L., Wilkinson, F.J. *Applied Optics* **24** (1985) 1531-1534.

7. Demas, J.N., Bowman, W.D., Zalewski, E.F., Velapoldi, R.A. *J. Phys. Chem.* **85** (1981) 2766-2771.

8. Jaworski, B.M., Detlaf, A.A. *Physik griffbereit*, Vieweg und Sohn, Braunschweig, 1972, pp. 567.

II. List of Actinometers

The present compilation lists chemical systems that have been shown suitable for the integration of incident light by chemical conversion. Emphasis is mainly on gas and liquid phase systems which photochemists are most frequently dealing with. In addition, some solid phase actinometers and convenient electronic devices are mentioned. Actinometric systems or procedures marked by an asterisk (*** = well established**) in the following list have been used over years by different authors in several laboratories and can thus be recommended (not necessarily, however, without precautions). All other systems appear to be not yet widely used and may be labelled **under discussion**. Systems that have fallen into discredit are given at the bottom of this list under the heading **Disproved.**

Readers are encouraged to send complementary information, corrections, and comments.

II.1. Chemical Systems

Several physical methods for the calibration of light sources (see sections I, II.2, and II.3) are known. With chemical systems, however, it is in general easier to mimic the experimental situation of the sample. By choosing strictly identical experimental set-ups for standard and sample, experimental errors due to differences in shape, surface, and spatial arrangement of the reaction vessel, filters, lenses, etc. can be avoided without much effort. The same solvent and equal absorbances should be chosen for actinometry and reaction under study, whenever possible. Corrections due to reflection losses at surfaces should be taken into account (see Section I.4.1). A recommended alternative (see Section I), especially for low photon densities at which multiphoton processes do not play a role, is to use a total absorbing actinometer solution (see Section I.4.4).

Order in the following lists is with increasing wavelength range. See the **Abbreviations** at the beginning of the document.

II.1.1. Solid Phase and Microheterogeneous Phase Chemical Actinometers

For solid-state quantum yield determination procedures *cf*., *e.g*.: Ito, Y., Matsuura, T. *J. Photochem. Photobiol. A: Chem*istry **50** (1989) 141-145; *Tetrahedron Lett*. **29** (1988) 3087-3090, 3091-3094; Zimmerman, H.E., Zuraw, M.J. *J. Am. Chem. Soc.* **111** (1989) 7974-7989.

For quantitative measurements in sol-gel materials see: Levy, D. *Chem. Mater.* **9** (1997) 2666-2670.

The references given below in the area of solid state chemical and biological dosimetry are not meant to cover this vast field as a whole but to give just some selected entry keys.

S01: *Uracil* photodimerization in polycrystalline thin layer.

Biological UV dosimeter

WR: > 250 nm.

AM: absorption spectrum 250 – 400 nm.

Phage T7 used as a calibration system.

1   Fisher, G.J., Johns, H. in*: Photochemistry and Photobiology of Nucleic Acids*, Vol.1 (Wang, S.Y., ed.), Academic Press, New York 1976, Ch.5, p.225-294.

2   Grof, P., Gaspar, S., Rontó, G. *Photochem. Photobiol.* **64** (1996) 800-806.

S02: *DNA* photodamaging, *e.g.*, on nylon membrane sealed in a polyethylene envelope.

Biological solar UV dosimeters.

WR: 254 – 330 nm

AM: immunostaining with damage-specific monoclonal antibody [1]

1.   Ishigaki, Y., Takayama, A., Yamashita, S., Nikaido, O. *J. Photochem. Photobiol. B: Biol.* **50** (1999)184-188, and refs. therein; some related "living dosimeters":

2.   *biofilm of Bac. subtilis spores,* Quintern, L.E., Horneck, G., Eschweiler, U., Bücker, H. *Photochem. Photobiol.* **55** (1992) 389-395.

3.   *special Escherichia coli bacteria strain K12 AB2480(uvrA⁻ recA⁻) with photodamage repair deficiency,* (193, 254 nm), Gurzadyan, G.G., Görner, H., Schulte-Frohlinde, D. *Radiation Research* **141** (1995) 244-251 and refs. therein, especially by Howard-Flanders, P. *et.al.*

4.   *cf.*, *e.g.*, *Special issue on biological dosimetry of UV radiation* (Fekete, A., Rontó, G., eds.): *J. Photochem. Photobiol. B: Biol.* **53** (1999).

S03: *1-Ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine-3-carboxylic acid (nalidixic acid).*

UV-A polyvinyl chloride film dosimeter

WR: 280 – 360 nm

AM: absorbance change at 330 nm

PP: very preliminary batch-dependent data

1.   Tate, T.J., Diffey, B.L., Davis, A. *Photochem. Photobiol.* **31** (1980) 27-30.

2.   Gibbs, N.K., Young, A.R. *Photochem. Photobiol.* **37** (1983) 345-348.

S04: *Thymine* dimerization.

UV-B radiation dosimeter in SDS microemulsions

WR: 290– 320 nm; $\Phi = 10^{-3} - 10^{-1}$ depending on [Thymine] and [SDS]/H$_2$O ratio

A TiO$_2$ -sol based actinometer used to determine number of photons absorbed.

AM: decrease of thymine absorption at 265 nm

Che, Y.S., Huang, J.S., Barnard, W., Li, Y.H. *Analyt. Chim. Acta* **318** (1995) 103-112.

S05: *Azoxybenzene* → 2-hydroxyazobenzene. *cf.* L22.

WR: 300 – 400 nm; poly(methyl methacrylate) block; $\Phi \sim 10^{-3}$

AM: absorbance at 420 nm

1. Bunce, N.J., Smith, J.J. *J. Photochem.* **23** (1983) 219-231.

2. Bunce, N.J., Debrabandere, G.G., Jacobs, K.B., Lemke, M.E., Montgomery, C.R., Nakai, J.S., Stewart, E.J. *J. Photochem.* **34** (1986) 105-115.

S06: *o-Nitrobenzaldehyde* → *o*-nitrosobenzoic acid photoisomerization.

WR: 310 – 400 nm; KBr pellet; $\Phi = 0.5$ (same in all phases)

WR: 280 – 410 nm; poly(methyl methacrylate); $\Phi = 0.5 \pm 0.06$

AM: IR 1530 cm^{-1} (NO$_2$ band disappearance)

1. Pitts, Jr., J.N., Wan, J.K.S., Schuck, E.A. *J. Am. Chem. Soc.* **86** (1964) 3606-3610.

2. Pitts, Jr., J.N., Hess, L.D., Baum, E.J., Schuck, E.A., Wan, J.K.S., Leermakers, P.A., Vesley, G. *Photochem. Photobiol.* **4** (1965) 305-321.

3. Cowell, G.W., Pitts, Jr., J.N. *J. Am. Chem. Soc.* **90** (1968) 1106-1110.

4. Leighton, P., Lucy, F.A. *J. Chem. Phys.* **2** (1934) 756-759.

5. Roy, C.B., Das, S.C. *Indian J. Chem.* **14A** (1976) 653-655.

6. Fleischmann, E.M. *Limnol. Oceanogr.* **34** (1989)1623-1629.; for the measurement and penetration of UV radiation into marine water (see also L35, [5]).

7. *also applicable in gas and liquid phase, cf. e.g.*, Allen, J.M., Allen, S.A., Dreiman, J., Baertschi, S.W. *Photochem. Photobiol.* **69** (1999) 17S-18S.

S07: *Polysulfone* UV-B film dosimeter.

WR: ≤ 315 nm

AM: absorbance change at 300 nm (ΔA_{300})

1. Davis, A., Diffey, B.L., Tate, T.K. *Photochem. Photobiol.* **34** (1981) 283-286.; ΔA_{300} mathematically correlates with the UV (300 nm) radiant exposure in kJ m^{-2}. Irradiance was measured using a vacuum thermopile.

2. Diffey, B.L. *Photochem. Photobiol.* **46** (1987) 55-60.; Quantitative erythemal effectiveness given *vs.* λ.; comparison of radiometric with actinometric measurements

3. Some related UV-A and B dosimeter system*s: polycarbonate plastic,* Wong, C.F., Fleming, R., Carter, S.J. *Photochem. Photobiol.* **50** (1989) 611-615.

4. *fuchsin and sandolan yellow dyes in polyvinyl alcohol polymer,* Rehim, F.A., Gawad, A.S.A., Fattah, A.A.A. *J. Photochem. Photobiol. A: Chemistry* **64** (1992) 123-131.

S08: *4a,7-Dimethyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione* (Diels-Alder adduct of 2.5-dimethylbenzoquinone and cyclopentadiene) photoisomerization in a dry silica matrix.

Irradiation apparatus described for adsorbed substances.

WR: 362 ± 5 nm; $\Phi = 1.0$ (*vs.* ferrioxalate, L31*; starting material disappearance and product appearance; also in solution)

AM: absorbance, GC

Lazare, S., de Mayo, P., Ware, W.R. *Photochem. Photobiol.* **34** (1981) 187-190.

S09: *2-(2-Quinolyl)-1.3-indanedione (quinophthalone)* photofading.

Plastic plates.

WR: 366 – 436 nm; Φ = 2 x 10^{-5}

AM: absorbance decrease at 420 nm

Okabe, H. *Appl. Opt.* **20** (1981) 4054-4058.

II.1.2. Gas Phase Chemical Actinometers

For reviews on UV and vacuum UV actinometers, *cf.* Pravilov, A.M. Gas-phase actinometry for UV and vacuum UV spectral regions, *High Energy Chem.* **21** (1987) 243-255, (Russian: *Khim. Vys. Energ.* **21**, 291-304) and Bercowitz, J. The quantum yield of ionization, *Physics Essays* **13** (2000) 248-255.

G01: *Rare gases* photoionization.

WR: 4.4 - 102.2 nm, Φ(ion) = 1 at infinitely low pressure

AM: He or Ne ion current measurement, extrapolation to zero pressure to correct for secondary ionization [1].

1. Samson, J.A.R., Haddad, G.N. *J. Opt. Soc. Amer.* **64** (1974) 47-54.
2. Saito, T., Onuki, H. *Metrologia*, **32** (1996) 525-529.
3. Bercowitz, J. *Physics Essays* **13** (2000) 248-255.

G02: *Nitrogen monoxide (NO)* photoionization.

WR: $\leq$ 134 nm , Φ_{λ} (ion) vary with λ, from 0.66 to 0.98 in the 58-75 nm region and are 0.3-0.6 in the 75-105 nm region [1].

AM: ion yield by photocurrent measurement, absolute photon fluences measured with a calibrated thermocouple.

1. Watanabe, K., Matsunaga, F.M., Sakai, H. *Appl. Opt.* **5** (1967) 391-396.
2. Bercowitz, J. *Physics Essays* **13** (2000) 248-255.

PP: The use of the traditional name nitric oxide is not recommended by IUPAC

G03*: *Dinitrogen oxide (N₂O)* photolysis.

WR: 147 – 185 (138 – 210) nm; $\Phi(\Delta n)$ = $\Phi(N_2)$ + $\Phi(O_2)$ + $\Phi(NO)$ - $\Phi(N_2O)$ = 1.00 ± 0.05; $\Phi(N_2)$ = 1.44 ± 0.1 at moderate pressure near room temperature;

$\Phi(N_2)$ = 1.18 at 123.6 nm [3]; $\Phi(\Delta n)$ ~ 0.8 at 105 – 120 nm [3]

AM: N_2 analysis, pressure measurement

PP: low absorbance at 150 – 170 nm ($\epsilon \leq 30$ $dm^3 mol^{-1} cm^{-1}$); separation of N_2 from NO and O_2 or very accurate pressure measurement. The use of the traditional name nitrous oxide is not recommended by IUPAC.

1. *cf.* Calvert, J.G., Pitts, Jr. J.N., *Photochemistry*, Wiley, New York 1966, p.782.
2. Zelikoff, M., Aschenbrand, L.M. *J. Chem. Phys.* **22** (1954) 1685-1687.
3. Groth, W.E., Schierholz, H. *Planet. Space Sci.* **1**(1959) 333-336.
4. Greiner, N.R. *J. Chem. Phys.* **47** (1967) 4373-4377.
5. Pravilov, A.M, Shul'pyakov, I.O. *High Energy Chem.* **19** (1985) 351-354.

6.   Dodge, M.C., Heicklen, J. *Int. J. Chem. Kinet.* **3** (1971) 269-282.

G04: *Oxygen* photolysis.

WR: 130 – 190 nm; $\Phi(O_3) = 2.0$ at low conversions and fast flow systems

AM: absorbance at 353 nm of iodine-iodide complex (formed from the produced ozone bubbled through a KI solution)

1.   *cf.* Calvert, J.G., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p.782.

2.   Driscoll, J.N., Warneck, P. *Photochem. Photobiol.* **13** (1971) 283-287.

3.   Powell, G.R., Sethi, D.S. *Int. J. Chem. Kinet.* **10** (1978) 1161-1166.

4.   Davies, A.K., Khan, K.A., McKellar, J.F., Phillips, G.O. *Mol. Photochem.* **7** (1976) 389-398.

G05: *Hexafluoroacetone* photolysis.

WR: 147 nm; $\Phi(CO) = 0.97 \pm 0.05$

AM: CO

1.   Magenheimer, J.J., Timmons, R.B. *J. Chem. Phys.* **52** (1970) 2790-2791.

2.   Powell, G.R., Sethi, D.S. *Int. J. Chem. Kinet.* **10** (1978) 1161-1166.

G06: *Ethene* photolysis.

WR: 147, 163, 185 nm; $\Phi(H_2) = 0.4$, independent of pressure, wavelength, and temperature

AM: H_2 analysis, pressure measurement

PP: care must be taken for $\lambda > 180$ nm [1]

1.   Glasgow, L.C., Potzinger, P. *J. Phys. Chem* **76** (1972) 138-140.

2.   Potzinger, P., Glasgow, L.C., von Bünau, G. *Z. Naturf.* **27a** (1972) 628-638.

3.   Okabe, H. *Photochemistry of Small Molecules*, Wiley-Interscience, New York 1978, p.126.

G07: *Trimethylamine* photoionization.

WR: 147 nm; $\Phi(\text{ion}) = 0.38$

AM: ion saturation current, very precise

Salomon, D., Scala, A.A. *J. Chem. Phys.* **62** (1975) 1469-1472.

G08: *Carbon dioxide* photolysis.

WR: below 170 nm; $\Phi(CO) = 0.5 – 1.06$ variable with λ

AM: CO analysis, oxygen formed must be separated

PP: complex system with interferences by O_3 and heterogeneous reactions on the walls

1.   *cf.* Calvert, J.G., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p.782.

2.   Warneck, P. *J. Opt. Soc. Amer.* **56** (1966) 408-409.

3.   Okabe, H. *Photochemistry of Small Molecules*, Wiley-Interscience, New York 1978, p.127.

G09*: *Hydrogen bromide* photolysis.

WR: 170 – 255 nm; $\Phi = 1$ (H_2 or Br_2) at 100 mm, 25 °C, at low conversion (< 1 %) due to interference by product Br_2.

AM: H_2 analysis, Hg interferes; Br_2 absorbance at 450 nm [3]

1.   *cf.* Calvert, J.G., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p.782.

2. Martin, R.M., Willard, J.E. *J. Chem. Phys.* **40** (1964) 2999-3007.

3. Roland, R.P., Bolle, M., Anderson, R.W. *J. Phys. D: Appl. Phys.* **31** (1998) 1336-1342.

G10: *Phosgene* photolysis.

WR: 200 – 280 nm; $\Phi(CO) = 1.0 \pm 0.1$ at 254 nm, 1 at 185 nm

AM: CO measurement at liquid nitrogen temperature.

1. Okabe, H. *Photochemistry of Small Molecules*, Wiley-Interscience, New York 1978, p.127.

2. Glicker, S., Okabe, H. *J. Phys. Chem.* **91** (1987) 437-440.

G11: *Nitrosyl chloride* photolysis.

WR: 230 – 630 nm; $\Phi(NO) \sim 2.0$

AM: NO analysis

1. *cf.* Calvert, J.G., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p.782.

2. Vilesov, F.I., Karpov, L.G., Kozlov, A.S., Pravilov, A.M., Smirnova, L.G. *High Energy Chem.* **12** (1978) 468-469.

3. Pravilov, A.M., Ryabov, S.E. *High Energy Chem.* **16** (1982) 331-333.

G12: *Perfluoroglutaryl dichloride* or *4-chloroperfluorobutanoyl chloride* (stable intermediate product) photolysis.

WR: 232 – 270 nm or 240 – 270 nm; $\Phi(CO) = 1.02 \pm 0.06$ and 1.03 ± 0.06, resp.

AM: GC for CO, $Cl(CF_2)_3COCl$, or $Cl(CF_2)_3Cl$.

PP: independent of total pressure, photon fluence, and λ.

Weibel, D.E., de Staricco, E.R., Staricco, E.H. *J. Photochem. Photobiol.* **54** (1990) 181-186.

G13*: *Acetone* photolysis.

WR: 250 – 320 nm; $\Phi(CO) = 1.0$ at ≥ 125 °C and ≤ 50 mm Hg

AM: pressure measurement and GC (CO and CH_4) after freezing down at −196 °C,

cf. Calvert, J.G., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p.782.

G14: *Acetone/hydrogen chloride* photolysis.

WR: 285, 300, 313 nm;

$\Phi(CH_4)/\Phi(CO) = 2$ at p(acetone) = 5 - 60 mm Hg, p(HCl) = 1 – 8 mm Hg, 130 °C

AM: GC or MS for CH_4 and CO

Horowitz, A. *J. Photochem.* **37** (1987) 241-246.

G15*: *Pentan-3-one* photolysis.

as G13, simple pressure measurement for CO after freezing down at −196 °C

G16: *But-2-ene*, Hg sensitized photoisomerization.

WR: 254 nm; $\Phi(cis{\to}trans) = \Phi(trans{\to}cis) = 0.50 \pm 0.02$ at $p \geq 4$ kPa

AM: GC

1. Cundall, R.B., Palmer, T.F. *Trans. Faraday Soc.* **56** (1960) 1211-1224.

2. Cundall, R.B., *Progr. Reaction Kinetics* **2** (1964) 165-215.

3. Termonia, M., De Maré, G.R. *Chem. Phys. Lett.* **25** (1974) 402-404.

G17: *Propane*, Hg-sensitized photolysis.

WR: 254 nm; $\Phi(H_2)$ = 0.581 at p = 40 kPa

AM: pressure measurement

1. Rousseau, Y. *Dissertation*, University of Alberta 1963.
2. Pollock, T.L. *Dissertation*, University of Alberta 1971.

G18: *Perfluoroacetic anhydride*.

WR: 254, 265 nm; $\Phi(CO)$ = 0.29 ± 0.02 at 25 °C, 0.34 at 20 °C

AM: CO measurement, Fourier transform infra-red (FTIR) spectroscopy.

1. Chamberlain, G.A., Whittle, E. *J. Chem. Soc. Faraday Trans.* I **71** (1975) 1978-1990.
2. Clemitshaw, K.C., Sodeau, J.R. *J. Photochem. Photobiol. A: Chemistry* **86** (1995) 9-14.

G19: *Perfluoropropionic anhydride*.

WR: 254, 265 nm; $\Phi(CO)$ = 0.24 at 26 °C, 0.29 at 200 °C

AM: CO measurement

1. Chamberlain, G.A., Whittle, E. *J. Chem. Soc. Faraday Trans.* I **71** (1975) 1978-1990.
2. *study of perfluorosuccinic anhydride photolysis:* Weibel, D.E., de Staricco. E.R., Staricco, E.H. *J. Photochem. Photobiol. A: Chem*istry **49** (1989) 279-285.

G20: *Azomethane*.

WR: 270 – 410 nm: $\Phi(N_2)$ = 1, independent of temperature (24-164 °C), fluence, and pressure

AM: N_2 must be isolated from the $N_2 + CH_4$ mixture

Okabe, H. *Photochemistry of Small Molecules*, Wiley-Interscience, New York etc., 1978, p.128.

G21: *Chlorine/hydrogen* chain photoinitiation.

WR: 280 – 380 nm; for Cl_2:O_2 = 1:1, $\Phi \sim$ 30 -36 (chain length between 15 and 18; absolute measurement of radiant power with thermoelements)

AM: Cl_2 consumption

1. Cremer, E., Margreiter, H. *Z. physikal. Chem. Leipzig* **199** (1952) 90-99.
2. Cremer, E., Margreiter, H. *Angew. Chem.* **64** (1952) 427.

G22: *Chlorine monofluoride*.

WR: vacuum UV up to 320 nm; $\Phi(ClF_3)$ = 1 at room temperature, independent of initial ClF pressure

AM: Absorption at 210 nm of produced ClF_3

Chebotarev, N.F. *Russ. J. Phys. Chem.* **60** (1986) 1105-1106 - *Chem. Abstr.* **105** (1986) 87729c.

II.1.3. Liquid Phase Chemical Actinometers

For additional literature *cf.* Appendix.

L01: *Water* photohomolysis (OH radical production) in methanol (0.2 – 0.3 M) solution.

WR: 172 nm Xe-excimer source; Φ = 0.42 ± 0.04

AM: GC analysis of methanol degradation and products, ethylene glycol, formaldehyde (2.4-DNPH, HPLC), formic acid;

DOC = dissolved organic carbon; calibration by cyclooctene actinometer, *cf.* L02.

Heit, G., Neuner, A., Saugy, P.-Y., Braun, A.M. *J. Phys. Chem. A* **102** (1998) 5551-5561.

L02*: *cis-Cyclooctene cis-trans* photoisomerization.

WR: 185 nm: $\Phi(cis{\rightarrow}trans)$ = 0.34 ± 0.02 in *n*-pentane (0.02 M);

WR: 172 nm (Xe-excimer source): $\Phi(cis{\rightarrow}trans)$ = 0.32, $\Phi(trans{\rightarrow}cis)$ = 0.44 [5]

AM: *trans*-cyclooctene analysis (GC, Ag complex)

PP: the 254 nm Hg line is ineffective

1.   Srinivasan, R., Ors, J.A. *J. Am. Chem. Soc.* **100** (1978) 7089-7091.
2.   Schuchmann, H.-P., von Sonntag, C., Srinivasan, R. *J. Photochem.* **15** (1981) 159-162.
3.   Weeke, F., Bastian, E., Schomburg, G. *Chromatographia* **7** (1974) 163-170.
4.   Adam, W., Oppenländer, T. *Photochem. Photobiol.* **39** (1984) 719-723.
5.   Heit, G., Neuner, A., Saugy, P.-Y., Braun, A.M. *J. Phys. Chem. A* **102** (1998) 5551-5561.

L03*: *Ethanol* photolysis (*Farkas actinometer*).

WR: 185 nm; $\Phi(H_2)$ = 0.4 in 5 M aqueous solution

AM: H_2 analysis (GC)

PP: Solution must be free of H atom scavengers like O_2 and acetaldehyde which implies low conversions

($\leq$ 0.1 %); Φ depends on the ethanol concentration; the 254 nm Hg line is ineffective; no temperature

dependence in the 15 – 40 °C range

1.   von Sonntag, C., Schuchmann, H.-P. *Adv. Photochem.* **10** (1977) 59-145, *ibid* 81 and refs. therein;
2.   von Sonntag, C. *Z. physikal. Chem. N. F.* **69** (1970) 292-304.
3.   Schuchmann, H.-P., von Sonntag, C. *J. Photochem.* **16** (1981) 289-295.
4.   Weeke, F., Bastian, E., Schomburg, G. *Chromatographia* **7** (1974) 163-170.
5.   Davies, A.K., Khan, K.A., McKellar, J.F., Phillips, G.O. *Mol. Photochem.* **7** (1976) 389-398.

L04: *Hydrogen azide (hydrazoic acid)* photolysis.

WR: 200 – 260 nm; Φ = 1.00 ± 0.05 in water

AM: absorbance (HN_3), N_2, NH_2OH

PP: HN_3 (**Caution, Explosive**) was prepared in solution from NaN_3 and $HClO_4$ immediately prior to

irradiation and no thermal decomposition was observed under the conditions applied

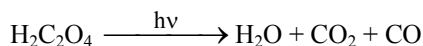Shapira, D., Treinin, A. *J. Phys. Chem.* **77** (1973) 1195-1198.

L05: *Glucose* photolysis.

WR: 200 – 300 nm; $\Phi \sim 0.33$ in 5 % aqueous solution

AM: absorbance of malonaldehyde/2-methylindole complex at 555 nm

Datta, R.K., Rao, K.N. *Indian J. Chem.* **14A** (1976) 122-123.

L06*: *Uranyl oxalate* photolysis.

$$H_2C_2O_4 \xrightarrow{h\nu} H_2O + CO_2 + CO$$

WR: 200 – 500 nm: $\Phi \sim 0.5 - 0.6$ in acidic aqueous solution

AM: $KMnO_4$ titration (rather insensitive at low conversion [9]) or absorbance at 320 nm of Ce(IV) after incubation (80 °C, 10 min) of photolysed solution with Ce(IV) sulfate in H_2SO_4 (*vs.* a non-irradiated blank), or GC (pH dependency [7,10]) for CO, CO_2 .

PP: use of commercial Ce(IV) sulfate for titration of non-photolysed $C_2O_4^{-2}$ is not recommended because ammonium nitrate impurities may limit the stability of the standardised solution. For the preparation of Ce(IV) *cf.* [12]; method depends critically on Ce(IV) concentration which should not be less than that of, and not higher than twice, the $C_2O_4^{-2}$ concentration of the blank.

1. Leighton, W.G., Forbes, G.S. *J. Am. Chem. Soc.* **52** (1930) 3139-3152.
2. Bracket, F.P., Forbes, G.S. *J. Am. Chem. Soc.* **55** (1933) 4459-4466.
3. Parker, C.A. *Proc. Roy. Soc. (London)*, **A220** (1953) 104-116.
4. Hatchard, C.G., Parker, C.A. *Proc. Roy. Soc.(London)*, **A235** (1956) 518-536.
5. Pitts, Jr., J.N., Margerum, J.D., Taylor, R.P., Brim, W. *J. Am. Chem. Soc.* **77** (1955) 5499-5501.
6. Discher, C.A., Smith, P.F., Lippman, I., Turse, R. *J. Phys. Chem.* **67** (1963) 2501-2503.
7. Volman, D.H., Seed, J.R. *J. Am. Chem. Soc.* **86** (1964) 5095-5098.
8. Calvert, J.G., Pitts, Jr. J.N., *Photochemistry*, Wiley, New York 1966, p. 787.
9. Murov, S.L. *Handbook of Photochemistry*, Dekker, New York, 2nd ed. 1993, sect.13, p.305.
10. Heidt, L.J., Tregay, G.W., Middleton, Jr., F.A. *J. Phys. Chem.* **74** (1970) 1876-1882; Porter, K., Volman, D.H. *J. Am. Chem. Soc.* **84** (1962) 2011-2012.
11. Taylor, H.A. in: *Analytical Photochemistry and Photochemical Analysis*, (Fitzgerald, J.M., ed.), Dekker, New York 1971, p. 91.
12. Eaton, D.F. *Ph.D. Thesis*, Calif. Institute of Technol., 1972, p.120.
13. de Mayo, P., Shizuka, H., *Creation and Detection of the Excited State* (Ware, W.R., ed.) **4** (1976) 140, Dekker, New York.
14. Smith, G.F., Fly, W.H. *Anal. Chem.* **21**, (1949) 1233-1237.
15. Benítez, F.J., Beltrán-Heredia, J., González, T., Acero, J.L. *Wat. Res*. **28** (1994) 2095-2100.
16. Rossetti, G.H., Albizzati, E.D., Alfano, O.M. *Ind. Eng. Chem. Res.* **37** (1998) 3592-3601.
17. Sánchez Mirón, A., Molina Grima, E., Fernández Sevilla, J.M., Chisti, Y., García Camacho, F. *J. Appl. Phycology* **12** (2000) 385-394.

PP: *Take care to dispose of the uranium waste in accordance with the legal regulations*.

L07: *4-(Dimethylamino)-α-[4-(dimethylamino)phenyl]-α-phenylbenzeneacetonitrile (malachite green leucocyanide)* photoionization in slightly acidified ethanol

WR: 225 – 289 nm (especially useful for very low fluences); $\Phi = 0.91 \pm 0.01$ (determined by using a thermopile for absolute measurement of fluences)

AM: absorbance at 620 nm

1. Calvert, J.G., Rechen, H.J.L. *J. Am. Chem. Soc.* **74** (1952) 2101-2103.

2. Fisher, G.J., LeBlanc, J.C., Johns, H.E. *Photochem. Photobiol.* **6** (1967) 757-767.

3. Taylor, H.A. in: *Analytical Photochemistry and Photochemical Analysis* (Fitzgerald, J.M., ed.), Dekker, New York 1971, p. 91-115.

PP: care should be taken to avoid product accumulation.

4. *on paper*: Chalkley, L. *J. Opt. Soc. Amer.* **42** (1952) 387-392.

5. *in thin films*: Nakazumi, H., Makita, K., Nagashiro, R. *J. Sol-Gel. Sc. Techn.* **8** (1997) 901-909.

L08: *Chloroacetic acid* photohydrolysis.

WR: $\leq$ 270 nm; Φ_λ = 0.31 at 254 nm (*vs.* other actinometers), 25 °C, temperature coefficient +0.009/°C in aqueous solution.

AM: product formation by potentiometry, polarography, turbidimetry, Cl^- ion specific electrode

1. Smith, R.N., Leighton, P.A., Leighton, W.G. *J. Am. Chem. Soc.* **61** (1939) 2299-2301.

2. Thomas, L.B. *J. Am. Chem. Soc.* **62** (1940) 1879-1880.

3. Kemula, W., Grabowska, A. *Roczn. Chemii* **29** (1955) 834-838.

4. Taylor, H.A. p. 91-115 in: *Analytical Photochemistry and Photochemical Analysis* (Fitzgerald, J.M. ed), Dekker, New York 1971.

5. Neumann-Spallart, M., Getoff, N. *Radiat. Phys. Chem.* **13** (1979) 101-105.

L09*: *Uridine (1-ß-D-ribofuranosyluracil)* photohydration in H_2O

WR: 216 – 280 nm; Φ_λ = 0.017 (238 nm), 0.019 (248 nm), 0.017 (265 nm), 0.016 (280 nm); Φ_λ = 0.034 (doubtful, conditions not given, applied to 222 nm excimer lamp, [9]); Φ_λ = 0.019 (254 nm, [4,6]; Φ_λ = 0.018 (254 nm, [8], fluence measured with a calibrated joulemeter); Φ_λ = 0.018 (216 nm laser, [8]); Φ_λ = 0.027, 0.032 (193 nm laser, Ar, [5]); Φ_λ = 0.044 (193 nm, Ar [8]);

AM: absorbance of uridine at 262 nm (chromophore loss), HPLC

PP: (1 – 1.5) x 10^{-4} – 10^{-5} M neutral aqueous solution; no effect of oxygen at 254 nm.

Φ_λ *ca.* 0.019 [1, 5, 6] refer to chromophore-loss due to photohydration; higher values [5, 8] at shorter λ (193 nm) are ascribed to additional ionization pathways and to dimerization reactions at higher concentrations.

1. Swenson, P.A., Setlow, R.B. *Photochem. Photobiol.* **2** (1963) 419-434.

2. Fisher, G.J., Johns, H. Ch.4, p.169-224 in*: Photochemistry and Photobiology of Nucleic Acids*, Vol.1 (Wang, S.Y., ed.), Academic Press, New York 1976.

3. Khoroshilova, E.V., Nikogosyan, D.N. *J. Photochem. Photobiol. B: Biol.* **5** (1990) 413-427.

4. Görner, H. *J. Photochem. Photobiol. B: Biol.* **10** (1991) 91-110.

5. Gurzadyan, G.G., Görner, H. *Photochem. Photobiol.* **60** (1994) 323-332.

6. von Sonntag, C., Schuchmann, H.-P. *J. Water SRT-Aqua* **41** (1992) 67-74.

7. Nohr, R.S., MacDonald, J.G., Kogelschatz, U., Mark, G., Schuchmann, H.-P., von Sonntag, C. *J. Photochem. Photobiol. A: Chemistry* **79** (1994) 141-149.

8. Gurzadyan, G.G., Görner, H. *Photochem. Photobiol.* **63** (1996) 143-153.

9. Zhang, J.-Y., Boyd, I.W., Esrom, H. *Applied Surface Science* **109/110** (1997) 482-486 – *Chem. Abstr.* 126-256881/19;

10. Linden, K.G., Darby, J.L. *J. Environm. Eng.* **123** (1997) 1142-1149.

L10: *1,3-Dimethyluracil* photohydration in aqueous solution.

WR: 240 – 280 nm; Φ_λ = 0.0130 ± 0.0007 in water (254 nm); 0.0140 (240 nm), 0.0111 (248 nm), 0.0138 (265 nm), 0.0147 (280 nm) at 0.9 mM in 0.01 M phosphate buffer, Φ(average) = 0.0134 ± 0.0016; at 6 x 10^{-5} M: Φ(average) = 0.0139 ± 0.0005

AM: absorbance at 266 nm

1. Fisher, G.J., Johns, H. in*: Photochemistry and Photobiology of Nucleic Acids*, Vol.1 (Wang, S.Y. ed), Academic Press, New York 1976, Ch.4, p.169-224.
2. Numao, N., Hamada, T., Yonemitsu, O. *Tetrahedron Lett.* (1977) 1661-1164.
3. Rahn, R.O., Sellin, H.G. *Photochem. Photobiol.* **30** (1979) 317-318.
4. Görner, H. *J. Photochem. Photobiol. B: Biol.* **10** (1991) 91-110.

L11*: *Azobenzene* [also called *Actinochrome 2R (245/440)*] photoisomerization (reusable).

WR: 230 – 460 nm; Φ(cis→trans) = 0.4 – 0.5; Φ(trans→cis) = 0.1 – 0.2 in methanol or isooctane; different for the two bands; *S* about 10^3 dm^3 mol^{-1} cm^{-1}.

AM: absorbance at 358 nm; HPLC

PP: 6.4 x10^{-4} M in CH$_3$OH; Φ(trans→ cis) = 0.14 in CH$_3$OH, 0.24 in isooctane; Φ(cis→trans) = 0.48 in CH$_3$OH, 0.55 in isooctane; commercial p.A. quality is sufficient, no side products, conversion limit 20 % (total absorption); no wavelength dependence of Φ for the *trans* → *cis* reaction; no temperature dependence; thermal *cis* → *trans* regeneration at 60 °C possible; reproducibility better than 2 %; also **applicable for lasers**

1. Zimmerman, G., Chow, L.-Y., Paik, U.-J. *J. Am. Chem. Soc.* **80** (1958) 3528-3531.
2. Gauglitz, G. *J. Photochem.* **5** (1976) 41-47.
3. Gauglitz, G., Hubig, S. *J. Photochem.* **15** (1981) 255-257.
4. Gauglitz, G., Hubig, S. *J. Photochem.* **30** (1985) 121-125.
5. Drabek, J., Cepciansky, I., Poskocil, J. *Chem. Listy* **78** (1984) 94-98.
6. Gauglitz, G., Hubig, S. *Z. Phys. Chem. N. F.* **139** (1984) 237-246.
7. Persy, G., Wirz, J. *EPA Newsletter* **29** (1987) 45-46.

PP: Quantum yields for the *cis* → *trans* reaction at 313 nm in various solvents were redetermined Φ = (0.35 ± 0.030) in acetonitrile, (0.37 ± 0.025) in methanol, (0.40 ± 0.035) in THF or 20 % ethanol/water, (0.40 ± 0.030) in cyclohexane, (0.44 ± 0.035) in *n*-hexane: Siampiringue, N., Guyot, G., Monti, S., Bortolus, P. *J. Photochem.* **37** (1987) 185-188.

8. application to polychromatic radiation (medium pressure Hg-arc plus filter solutions): Gahr, A., Weil, L., Nießner, R. *Water Res.* **29** (1995) 2125-2137.

L12: *1-Deazapurine 3-oxide (imidazo[4,5-b]pyridine 4-oxide)* or *1-methyl-1-deazapurine 3-oxide (6-methyl-imidazo[4,5-b]pyridine 4-oxide)* fluorogenic photorearrangement.

WR: 250 – 310 nm; 1 mM solutions in 10 mM phosphate buffer, pH 7; Φ = 0.13 – 0.15 (± 0.01 – 0.02) at 250, 254, 265, 280, 295, and 310 nm.

AM: fluorometric estimation (excitation at 340 nm, emission at 375 nm) of product 1-deazapurin-2-one or 1-methyl analog.

Blaney, R., Al-Nakib, T., Davies, R.J.H. *Photochem. Photobiol.* **57** (1993) 380-382.

L13*: *Potassium peroxodisulfate/tert-butyl alcohol* in oxygen-saturated aqueous solution.

WR: 254 nm, $\Phi = 1.8 \pm 0.2$ at 20 °C (H$^+$ production); at other temperatures (θ): $\Phi = 1.5 + 0.015\theta$; standard deviation $< \pm$ 5 %; independent of photon irradiance between $5 \times 10^{-6} - 2 \times 10^{-5}$ einstein m^{-2} s^{-1}.

AM: pH measurement and/or titration; or irradiation under pH monitoring up to the equivalence point (consumption of pre-added base sodium borate).

PP: freshly prepared oxygenated actinometer solution: 10 mM K$_2$S$_2$O$_8$ and 0.1 M tert-butanol; system developed for use in waterworks; only basic laboratory equipment required. However, exact calibration of pH instrument necessary in the 2 – 5 range; tert-butanol is essential (no other alcohol); lack of oxygen leads to lower Φ values; working range 10 – 25 °C, above 25 °C higher Φ values due to thermal decomposition of the peroxo salt.

1. Mark, G., Schuchmann, M.N., Schuchmann, H.-P., von Sonntag, C. *J. Photochem. Photobiol. A: Chem*istry **55** (1990) 157-168.

2. Mark, G., Schuchmann, M.N., Schuchmann, H.-P., von Sonntag, C. *J. Water SRT-Aqua* **39** (1990) 309-313.

3. Hoyer, O., Kryschi, R., Piecha, I., Mark, G., Schuchmann, M.N., Schuchmann, H.-P., von Sonntag, C. *J. Water SRT-Aqua* **41** (1992) 75-81.

L14: *Potassium iodide* in *dinitrogen oxide (N₂O)*-saturated aqueous solution.

WR: 254 nm, $\Phi = 0.235$ at 25 °C in aqueous solution, temperature (θ) dependence = +0.004 (θ-25) [°C]

AM: absorbance at 352 nm of triiodide

PP: 0.15 M KI in 0.1M borate buffer pH 4, N$_2$O bubbling (electron scavenger); gradual decrease (1-2 % per hour) of triiodide.

Rahn, R.O. *Photochem. Photobiol.* **58** (1993) 874-880.

PP: The use of the traditional name nitrous oxide is not recommended by IUPAC.

L15: *Potassium iodide/potassium iodate* in aqueous solution.

WR: 254 nm, $\Phi = 0.73 \pm 0.02$ (determined against a calibrated radiometer [3]) at 20.7 °C

AM: absorbance at 352 nm of triiodide ion, of iodide at 300 nm

PP: 0.6 M iodide and 0.1 M potassium iodate (electron scavenger) in 0.01 M borate buffer at pH 9.25; no bubbling necessary, but **note** concentration and temperature dependence; Φ_λ increases at $\lambda < 254$ nm and decreases at $\lambda > 254$ nm [3].

1. Rahn, R.O. *Photochem. Photobiol.* **66** (1997) 450-455; **erratum**: *ibid* **66** (1997) 885.

2. Rahn, R.O., Xu, P., Miller, S.L. *Photochem. Photobiol.* **70** (1999) 314-318.

3. Rahn, R.O., Stephan, M.I., Bolton, J.R., Goren, E., Shaw, P.-S., Lykke, K.R. *Photochem. Photobiol.* **78** (2003) 146-152.

L16: *1.1-Diphenylsilacyclobutane* photolysis.

WR: 254 nm, $\Phi = 0.21 \pm 0.03$ in deoxygenated methanolic hexane

AM: GC analysis of diphenylmethoxymethylsilane (trapping of primary product 1.1-diphenylsilene, besides ethene)

1. Leigh, W.J., Bradaric, C.J., Kerst, C., Banisch, J.H. *Organometallics* **15** (1996) 2246-2253.

2. Leigh, W.J., Boukherroub, R., Bradaric, C.J., Cserti, C.C., Schmeisser, J.M. *Can. J. Chem.* **77** (1999) 1136-1147.

L17: *1,3-Cycloheptadiene* photoisomerisation.

WR: 254 nm; $\Phi = 0.48 \pm 0.01$ in ethanol

AM: absorbance at 246 nm

Numao, N., Hamada, T., Yonemitsu, O. *Tetrahedron Lett.* (1977) 1661-1664.

L18: *Iodomethane* photoexchange with $^{132}I_2$.

WR: 254 nm; $\Phi = 1.0$

AM: radiochemical

1. Harris, G.M., Willard, J.E. *J. Am. Chem. Soc.* **76** (1954) 4678-4687.
2. Majer, J.R., Simons, J.P. *Adv. Photochem.* **2** (1964) 137-181.

L19: *1,2,3,4-Tetraphenylcyclobutane* (TPCB) photocycloreversion.

WR: 250 – 270 nm, continuous irradiation or 266 nm **laser** flashes ($< 10^{17}$ photons per pulse); $\Phi = 0.29 \pm 0.01$ in *n*-butyl chloride or methylcyclohexane (MCH)

AM: absorbance at 295 nm (*trans*-stilbene)

PP: no effect of temperature (270 – 310 K, MCH) or dissolved oxygen (MCH)

1. Takamuku, S., Beck, G., Schnabel, W. *J. Photochem.* **11** (1979) 49-52.
2. Murata, K., Yamaguchi, Y., Shizuka, H., Takamuku, S. *J. Photochem. Photobiol. A: Chemistry* **60** (1991) 207-214.

L20: *2.4-Dimethoxy-6-phenoxy-s-triazine* (DMPT) photo-*Fries* rearrangement

WR: 250 – 270 nm, continuous irradiation or 266 nm **laser** flashes ($< 10^{17}$ photons per pulse); $\Phi = 0.12 \pm 0.01$ in ethanol and 0.15 ± 0.01 in methylcyclohexane, no effect of oxygen

AM: absorbance at 331 nm of product 2.4-dimethoxy-6-(2-hydroxyphenyl)-s-triazine (besides 4-OH isomer) .

Murata, K., Yamaguchi, Y., Shizuka, H., Takamuku, S. *J. Photochem. Photobiol. A: Chemistry* **60** (1991) 207-214.

L21: *8H,16H-4b,12b-Epidioxydibenzo[a,j]perylene-8.16-dione [heterocoerdianthrone endoperoxide,* also called *Actinochrome 1R (248/334)]* photoreversible photodissociation.

WR: 248 – 334 nm for the dissociation; $\Phi = 0.27 \pm 0.01$ in dichloromethane (2×10^{-3} M) independent of λ between 253 and 302 nm; $S = (7770 \pm 200)$ $dm^3\, mol^{-1}\, cm^{-1}$ (253 – 302 nm), $S_\lambda = 7050, 6740,$ and 4630 $dm^3\, mol^{-1}\, cm^{-1}$ at 248, 313, and 334 nm, respectively, all at 23 ± 2 °C

AM: absorbance at 572 nm

PP: temperature coefficient +0.2 %/ °C; conversion limit ≤ 1 %; suitable as polychromatic quantum counter; solutions recover on exposure to sunlight behind a 455 nm cut-off filter and may be reused ~ 100 times without loss in accuracy. Actinometric use of the reverse reaction [3] is no longer recommended by the authors, since there are more convenient systems available for this wavelength region. Unfortunately, the compound is no longer commercially available.

1. Brauer, H.-D., Schmidt, R. *Photochem. Photobiol.* **37** (1983) 587-591.
2. Schmidt, R., Brauer, H.-D. *J. Photochem.* **25** (1984) 489-499.
3. Brauer, H.-D., Drews, W., Schmidt, R., Gauglitz, G., Hubig, S. *J. Photochem.* **20** (1982) 335-340.
4. Jesse, K., Comes, F.J., Schmidt, R., Brauer, H.-D. *Chem. Phys. Lett.* **160** (1989) 8-12.

L22: *Azoxybenzene* $\Rightarrow$ 2-hydroxyazobenzene photorearrangement.

In solid phase *cf.* S05

WR: 250 – 350 nm: $\Phi \sim$ 0.02 in ethanol, moderately dependent on λ

AM: absorbance at 458 nm in ethanolic KOH

PP: no concentration dependence; no temperature dependence up to at least 45 °C;

1. Bunce, N.J., LaMarre, J., Vaish, S.P. *Photochem. Photobiol.* **39** (1984) 531-533.

2. *cf.* Mauser, H., Gauglitz, G., Stier, F. *Liebigs Ann. Chem.* **739** (1970) 84-94.

L23: *3-(2-Hydroxyphenyl)-2-propenoic acid (o-coumaric acid dianion)* photoisomerization in aqueous solution

cis → *trans* reaction

WR: 254 – 300 nm: $\Phi(cis{\rightarrow}trans)$ = 0.52 ± 0.05; 313 – 400 nm: $\Phi(cis{\rightarrow}trans)$ = 0.75 ± 0.05

trans → *cis* reaction

WR: 254 – 300 and 350 – 400 nm: $\Phi(trans{\rightarrow}cis)$ = 0.10 ± 0.01

AM: absorbance, fluorescence at 492 nm

PP: Not recommended as a reliable actinometer; strong dependence on pH, O_2, and counterion (Cl⁻) concentration.

1. Perbet, G., Coulangeon, L.-M., Boule, P., Lemaire, J. *J. Chim. Phys.* **75** (1978) 1096-1104.

2. Guyot, G., Pizzocaro, C., Lemaire, J. *J. Photochem.* **36** (1987) 11-26.

L24: *Adenine* photolysis.

WR: 254 – 300 nm; Φ = 0.0027 – 0.0029 (deoxygenated), 0.0081 – 0.0085 (aerated); Φ (chromophore loss) $\approx 0.1 \times 10^{-3}$ (254 nm, Ar or O_2, [2])

AM: absorbance at 260 nm

PP: 4×10^{-5} M aqueous solution; student experiment, [1]; 2×10^{-5} M, [2]

Not recommended as a reliable actinometer, general dependence on concentration, oxygen, wavelength, and pH, [2]

1. Rivera, M. *J. Chem. Educ.* **66** (1989) 1049-1051.

2. *193 nm laser and 254 nm continuous irradiation*: Gurzadyan, G.G., Görner, H. *Photochem. Photobiol.* **60** (1994) 323-332.

L25: *2-Hydroxy-4'-(dimethylamino)chalcone* to 4'-(dimethylamino)flavylium ion photoconversion.

WR: 254 – 366 nm; Φ_λ = 0.23 ± 0.01 (366 nm), 0.21 (334 nm), 0.23 (313 nm), 0.16 (254 nm) at 20 °C, in acidic THF (99.5 % purity) solution.

AM: absorbance near 450 nm

PP: 0.075 – 10.0 mM chalcone, 5 mM p-toluenesulphonic acid (necessary for ring closure), water content of THF well below 0.4 %; water decreases quantum yield; strong effects of solvent and acidity; thermal bleaching of photoproduct at 50 °C; no photoreversion, negligible effect of oxygen.

1. Matsushima, R., Suzuki, N., Muarakami, T., Morioka, M. *J. Photochem. Photobiol. A: Chem*istry **109** (1997) 91-94.

2. *cf.* Matsushima, R., Mizuno, H., Kajiura, A. *Bull. Chem. Soc. Jpn.* **67** (1994) 1762-1764.

L26: *Stilbenes cis* → *trans* photoisomerization.

WR: 254 – 366 nm; quantum yields depend on stilbene substitution and solvent

AM: absorbance, GC

1. Saltiel, J., Marinari, A., Chang, D.W.-L., Mitchener, J.C., Megarity, E.D. *J. Am. Chem. Soc.* **101** (1979) 2982-2996.

2. Saltiel, J., Charlton, J.L. in: *Rearrangements in Ground and Excited States* (de Mayo, P., ed.) **3**, Academic Press,

New York 1980, p 25-90.

3.   Görner, H. *Ber. Bunsenges. Phys. Chem.* **88** (1984) 1199-1208

4.   Ho, T.-I., Su, T.-M., Hwang, T.-C. *J. Photochem. Photobiol. A: Chemistry* **41** (1988) 293-298.

L27: *1,2-Dimethoxy-4-nitrobenzene* → 2-methoxy-5-nitrophenolate anion, photohydrolysis.

WR: 254 – 365 nm (applied to 308 nm XeCl-excimer lamp, ref.2); $\Phi = 0.116 \pm 0.002$ (0.136 mM in 0.5 M aqueous KOH)

AM: absorbance of product 2-methoxy-5-nitrophenolate anion

1.   Pavlickova, L., Kuzmic, P., Soucek, M. *Coll. Czech. Chem. Comm.* **51** (1986) 368-374.

2.   Zhang, J.-Y., Esrom, H., Boyd, I.W. *Appl. Surf. Sci.* **138-139** (1999) 315-319 – *Chem. Abstr.* **130** 259437.

L28: *p-Benzoquinone* photoreduction in aqueous solution.

WR: 260 – 380 nm, $\Phi = 0.47 \pm 0.04$, pH 7, $(0.3 – 1) \, 10^{-3}$ M in 5×10^{-3} M phosphate buffer.

 AM: transient absorption at 430 nm (flash photolysis) of p-benzosemiquinone radical anion; EPR

1.   Ononye, A.I., Bolton, J.R. *J. Phys. Chem.* **90** (1986) 6270-6274.

2.   Ho, T.L., Bolton, J.R., Lipczynska-Kochany, E. *J. Adv. Oxid. Technol.* **1** (1996) 170-178.

PP: See however, von Sonntag, J., Mvula, E., Hildenbrand, K., von Sonntag, C. *Chem. Eur. J.* **10** (2004) 440-451.

L29: *Phenylglyoxylic acid* photodecarboxylation.

WR: 254 – 405 nm; $\Phi = 0.6 – 0.8$ in acidic acetonitrile-water (3:1 v/v) solution.

AM: absorbance at 360 – 390 nm, potentiometry, HPLC, NMR

PP: moderately dependent on λ; strongly dependent on pH and water content. Reproducibility better than ± 0.05; correction for product benzaldehyde content at $\lambda_{obs} \leq 370$ nm is necessary; not to be used above 45 °C; temperature (θ) coefficient $\Delta\Phi/\Delta\theta = 0.0029 \pm 0.0007/$ °C; conversion limit about 20 %; no significant dependence on air, concentration or radiant power; freshly recrystallized acid should be used.

1.   Defoin, A., Defoin-Straatmann, R., Hildenbrand, K., Bittersmann, E., Kreft, D., Kuhn, H.J. *J. Photochem.* **33** (1986) 237-255.

2.   Defoin, A., Kuhn, H.J. *EPA Newsletter* **26** (1986) 23-25.

3.   Kuhn, H.J., Görner, H. *J. Phys. Chem.* **92** (1988) 6208-6219.

4.   *photorheological effects in micellar solution:* Wolff, T., Schmidt, F., von Bünau, G. *J. Photochem. Photobiol. A: Chemisry* **48** (1989) 435-446.

L30: *Hydrogen peroxide* photolysis sensitized by uranyl sulfate.

WR: 250 – 450 nm; $\Phi = 1.30 \pm 0.03$ (20 °C) in 3 M H_2SO_4; temperature coefficient +0.0095/ °C

AM: O_2 volumetric, H_2O_2 consumption

1.   Schenck, G.O., Haubold, W. *referred to in*: Schenck, G.O. *Angew. Chem.* **69** (1957) 579-599.

2.   Folcher, G., Paris, J., Saito, E. *Nouv. J. Chim.* **7** (1983) 703-709.

3.   *cf.* Nicole, I., DeLaat, J., Dore, M., Duguet, J.P., Bonnel, C. *Water Res*. **24** (1990) 157-168.

4.   for primary Φ of H_2O_2 decomposition: *cf.* Weeks, J.L., Matheson, M.S. *J. Am. Chem. Soc.* **78** (1956) 1273-1278; Dainton, F.S. *J. Am. Chem. Soc.* **78** (1956) 1278-1279; Ho, T.L., Bolton, J.R., Lipczynska-Kochany, E. *J. Adv. Oxid. Technol.* **1** (1996) 170-178.

PP: *Take care to dispose of the uranium waste in accordance with current legal regulations.*

L31*: *Potassium tris(oxalato)ferrate(III) (potassium iron(III) oxalate*, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$) photoreduction (*Hatchard-Parker actinometer*). The most widely accepted standard actinometer, commonly called ferrioxalate actinometer.

WR: 250 – 500 nm; Φ = 1.25 – 0.9

AM: absorbance at 510 nm of Fe(II)-1.10-phenanthroline complex in buffered acidic solution

PP: See [36] for possible wavelength dependence in the 240-280 nm range.

PP: all work must be done under dark red light; pure solid green $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, recrystallized from water is stable in the dark; 0.006 – 0.20 M solutions have been used; only freshly prepared and mixed solutions should be used; make sure that there is total absorption; sufficient stirring is essential; complexation should be done immediately after irradiation; add irradiated solution to pre-mixed buffer-phenanthroline solution; complete complexation takes about an hour; phenanthroline solution is sensitive to UV (fluorescent room lights) and should be stored in the dark; in case of high conversion there may not be sufficient phenanthroline to complex all Fe(II); test for the linearity of the results with irradiation time; for use with **lasers** [19,22,33]; no problems at 60 °C without deoxygenation.

PP: In view of the numerous different and often contradictory observations and recommendations given in the literature concerning the adequate use of this actinometer it is suggested that publications contain a short but unequivocal indication as to which experimental conditions have been applied.

1. Hatchard, C.G., Parker, C.A.A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer, *Proc. Roy. Soc. (London)*, **A235** (1956) 518-536. part I: Parker, C.A. *Proc. Roy. Soc. (London)*, **A220** (1953) 104-116.

2. Baxendale, J.H., Bridge, N.K. Photoreduction of ferric compounds in aqueous solutions, *J. Phys. Chem.* **59** (1955) 783-788.

3. Bricker, C.E., Schonberg, S.S. Photometric determinations of Vanadium and Chromium, *Anal. Chem.* **30** (1958) 922-928.

4. Lee, J., Seliger, H.H. Quantum yield of ferrioxalate actinometer, *J. Chem. Phys.* **40** (1964) 519-523.

5. Calvert, J., Pitts, Jr., J.N. *Photochemistry*, Wiley, New York 1966, p. 783.

6. Wegner, E.E., Adamson, A.W. Photochemistry of complex ions. III. Absolute quantum yields for the photolysis of some aqueous chromium(III) complexes. Chemical actinometry in the long wavelength visible region, *J. Am. Chem. Soc.* **88** (1966) 394-404.

7. Wolf, H.P., Bohning, J.J., Schnieper, P.A., Weiss, K. Apparatus for the measurement of quantum yields and rates of photochemical reactions, *Photochem. Photobiol.* **6** (1967) 321-329.

8. Parker, C.A. *Photoluminescence of Solutions*, Elsevier, Amsterdam 1968, p. 208-214.

9. Taylor, H.A. Analytical methods and techniques for actinometry, in *Analytical Photochemistry and Photochemical Analysis,* (Fitzgerald, J.M., ed.), Dekker, New York 1971, p. 91-115.

10. Kurien, K.C. A modification to the ferrioxalate actinometer, *J. Chem. Soc.* B, (1971) 2081-2082.

11. Wrighton, M.S., Witz, S. Stability of Fe(II) in ferrioxalate solutions, *Mol. Photochem.* **3** (1972) 387-394.

12. Murov, S.L. *Handbook of Photochemistry*, Dekker, New York 1973, p. 119, 2nd ed. 1993, sect.13, p.299-313.

13. de Mayo, P., Shizuka, H. Measurement of reaction quantum yields, *Creation and Detection of the Excited State,* (Ware, W.R., ed.) **4** (1976) 139-216.

14. Bowman, W.D., Demas, J.N. Ferrioxalate actinometry. A warning on its correct use, *J. Phys. Chem.* **80** (1976) 2434-2435.

15. Nicodem, D.E., Cabral, M.L.P.F., Ferreira, J.C.N. The use of 0.15 M potassium ferrioxalate as a chemical actinometer, *Mol. Photochem.* **8** (1977) 213-238.

16. Thomas, P., Benedix, M., Hennig, H. Zur Synthese und Photolyse von Trisphenanthrolinium-trisoxalato-eisen(III) und seiner Eignung als Aktinometersubstanz, *Z. Chem.* **17** (1977) 114-115.

17. Fernández, E., Figuera, J.M., Tobar, A. Use of the potassium ferrioxalate actinometer below 254 nm, *J. Photochem.* **11** (1979) 69-71.

18. Baker, A.D., Casadavell, A., Gafney, H.D., Gellender, M. Photochemical reactions of tris(oxalato)iron (III), a first-year chemistry experiment, *J. Chem. Educ.* **57** (1980) 314-315.

19. Gruter, H. Measuring the pulse energy of a nitrogen laser with a potassium ferrioxalate actinometer, *J. Appl. Phys.* **51** (1980) 5204-5206.

20. Connolly, J.S., Meyer, T.H. A convenient irradiation cell for ferrioxalate actinometry, *Photochem. Photobiol.* **34** (1981)145-146.

21. Vitz, E.W., Boschmann, E. The ferrioxalate actinometer: A lecture demonstration, *J. Chem. Educ.* **58** (1981) 655.

22. Demas, J.N., Bowman, W.D., Zalewski, E.F., Velapoldi, R.A., Determination of the quantum yield of the ferrioxalate actinometer with electrically calibrated radiometers, *J. Phys. Chem.* **85** (1981) 2766-2771.

23. Langford, C.H., Holubov, C.A. Wavelength and temperature dependence in the photolysis of the chemical actino-meter, potassium trisoxalatoferrate(III), at longer wavelengths, *Inorgan. Chim. Acta* **53** (1981) L59-L60.

24. Wolfenden, E.A., Agnew, A.D.Q., Causton, D.R. A photochemical light meter suitable for ecological survey, *Acta Oecolog. Oecol. Plant.* **3** (1982) 101-111.

25. Nicodem, D.E., Aquilera, O.M.V. Standardization of the potassium ferrioxalate actinometer over the temperature range 5 – 80 °C, *J. Photochem.* **21** (1983) 189-193.

26. Kirk, A.D., Namasivayam, C. Errors in ferrioxalate actinometry, *Anal. Chem.* **55** (1983) 2428-2429.

27. Gauglitz, G. Modern chemical actinometry, *EPA Newsletter* **19** (1983) 49-53.

28. Fischer, E. Ferrioxalate actinometry, *EPA Newsletter* **21** (1984) 33-34.

29. Braun, A.M., Maurette, M.-T., Oliveros, E. *Technologie Photochimique*, Presses Polytechniques Romandes, Lausanne 1986, p. 43 - 96; *idem, Photochemical Technology*, John Wiley & Sons Ltd. Chichester, 1991, p 77-81.

30. Vincze, L., Papp, S. Individual quantum yields of $(Fe^{3+}OX_n^{2-}H_m)^{+\bullet}$ complexes in aqueous acidic solutions ($OX^{2-} \equiv C_2O_4^{2-}$, n = 1 – 3, m = 0.1), *J. Photochem.* **36** (1987) 289-296.

31. Harris, G.D., Adams, V.D., Moore, W.M., Sorensen, D.L. Potassium ferrioxalate as chemical actinometer in ultraviolet reactors, *J. Environ. Eng.* **113** (1987) 612-627.

32. Timpe, H.-J., Ulrich, S., Ali, S. Spin-trapping as a tool for quantum yield determinations in radical forming processes, *J. Photochem. Photobiol. A: Chemistry* **61** (1991) 77-89. (actinometry in an ESR tube).

33. Izumi, Y. *et al.*, Actinometry of an excimer laser with a ferrioxalate chemical actinometer, *Reza Kenkyu* **19** (1991) 247-253 – *Chem. Abstr.* **115** 193378/18.

34. Sun, L., Bolton, J.R. Determination of the quantum yield for the photochemical generation of hydroxyl radicals in TiO_2 suspensions (heterogeneous soln., integrating sphere assembly, actin. in an EPR flat cell), *J. Phys. Chem.* **100** (1996) 4127-4134.

35. Vincze, L., Kemp, T.J., Unwin, P.R. Flow actinometry in a thin film reactor: modeling and measurements*, J. Photochem. Photobiol. A: Chemistry* **123** (1999) 7-13.

36. Rahn, R.O., Stefan, M.I., Bolton, J.R., Goren, E., Shaw, P.-S., Lykke, K.R. Quantum yield of the iodide/iodate actinometer: dependence of wavelength and concentration (possible wavelength dependence of the ferrioxalate actinometer in the 240-280 nm range), *Photochem. Photobiol.* **78** (2003) 146-152.

L32*: <u>Laser</u> pulse actinometry via *standard transients*.

WR: 265 – 532 nm in various solvents (depending on the substance used)

AM: transient absorbance

1. 265 nm (*anthracene* in hexane, *naphthalene* in cyclohexane) Bensasson, R., Goldschmidt, C.R., Land, E.J., Truscott, T.G. *Photochem. Photobiol.* **28** (1978) 277-281.

2. 308 nm: (*benzophenone-4-carboxylate* in aqueous solution): von Sonntag, J. *J. Photochem. Photobiol. A: Chemistry* **126** (1999)1-5.

3. 308 nm , 355 nm (*benzophenone, benzoins*): García, C., Smith, G.A., McGimpsey, W.G., Kochevar, I.E., Redmond, R.W. *J. Am. Chem. Soc.* **117** (1995) 10871-10878; Shestra, N.K., Yagi, E.J., Takatori, Y., Kawai, A., Kajii, Y., Shibuya, K., Obi, K. *J. Photochem. Photobiol. A: Chemistry* **116** (1998) 179-185.

4. 337 nm (*benzophenone-4-carboxylate* in aqueous solution): Marciniak, B., Andrzejewska, E., Hug, G.L. *J. Photochem. Photobiol. A: Chemistry* **112** (1998) 21-28.

5. 347 nm (*benzophenone, ZnTPP* in toluene and other solvents): Romashov, L.V., Kiryukhin, Yu.I., Bagdasar'yan, Kh.S *High Energy Chem.* **12** (1978) 132-134; Carmichael, I., Hug, G.L. *J. Phys. Chem. Ref. Data* **15** (1986) 1-250; Hurley, J.K., Sinai, N., Linschitz, H. *Photochem. Photobiol.* **38** (1983) 9-14.

6. 347 nm: (*benzophenone-4-carboxylate* in aqueous solution): Hurley, J.K., Linschitz, H., Treinin, A. *J. Phys. Chem.* **92** (1988) 5151-5159.

7. 353 nm (*all-trans-retinal* in hexane): Bensasson, R., Goldschmidt, C.R., Land, E.J., Truscott, T.G. *Photochem. Photobiol.* **28** (1978) 277-281.

8. 355 nm, 532 nm [$Ru(bpy)_3^{2+}$ in aqueous solutions and polar organic solvents]: Yoshimura, A., Hoffman, M.Z., Sun, H. *J. Photochem. Photobiol. A: Chemistry* **70** (1993) 29-33.

9. *cf.* Bonneau, R., Carmichael, I., Hug, G.L. Molar absorption coefficients of transient species in solution, *Pure Appl. Chem.* **63** (1991) 289-299.

10. *cf.* Bonneau, R., Wirz, J., Zuberbühler, A.D. Methods for the analysis of transient absorbance data, *Pure Appl. Chem.* **69** (1997) 979-992.

see: http://www.rcdc.nd.edu/browse_compil.html#browse_access

L33: *2,3-Dimethylbut-2-ene*, sensitized photooxygenation.

Especially designed for <u>high-power pulse and cw lasers.</u>

WR: 280 – 560 nm; $\Phi = 0.76 \pm 0.03$ with methanolic $Ru(bpy)_3^{2+}$ *chloride* and *2,3-dimethyl-2-butene* as acceptor, in the presence of O_2 in a sealed cuvette

AM: O_2 consumption, volumetric

PP: slight dependence of Φ_{obs} on 2,3-dimethyl-2-butene concentration and oxygen pressure

1. Demas, J.N., Harris, E.W., McBride, R.P. in: *Lasers in Physics, Chemistry, and Biophysics, Proc. Int. Meet. Soc. Chim. Phys.* **27**, (Joussot-Dubien, J., ed.), Elsevier, Amsterdam, 1975, p.477-484.

2. Demas, J.N., McBride, R.P., Harris, E.W. *J. Phys. Chem.* **80** (1976) 2248-2253.

L34: *Iodide* photooxidation in aerated aqueous buffered solution

WR: Rose Bengal sensitization

AM: amperometric detection of I_2 or redox titration of iodine

PP: efficiency of I_2 formation depends on pH and temperature

Method applied for the analytical determination of I_2 reducing substances

Sánchez-Pedreño, C., Pérez-Ruiz, T., Martínez-Lozano, C., Hernández-Córdoba, M. *Analyt. Chim. Acta* **104** (1979) 397-402.

L35: *o-Nitrobenzaldehyde* $\rightarrow$ *o*-nitrosobenzoic acid photoisomerization.

WR: 300 - 410 nm; Φ = 0.5 in acetone and Cl_2CH_2, independent of temperature. Same Φ in all phases (*cf.* S06).

AM: GC; LC; IR NO_2 band disappearance

1. Leighton, P., F.A. Lucy, *J. Chem. Phys.* **2** (1934) 756-759.
2. Pitts, Jr., J.N., Vernon, J.M., Wan, J.K.S. *Int. J. Air Water Pollut.* **9** (1965) 595-600.
3. Willett, K.L., Hites, R.A. *J. Chem. Ed.* **77** (2000) 900-902.
4. Allen, J.M., Allen, S.A., Dreiman, J., Baertschi, S.W. *Photochem. Photobiol.* **69** (1999) 17S-18S; when the reaction is carried out in the presence of NaOH, the pH of the solution serves as a measure of the degree of photoisomerization.
5. Morales, R.G.E., Jara, G.P., Cabrera, S. *Limnol. Oceanogr.* **38** (1993) 703-705; for the determination of solar UV radiation and penetration in waters.
6. von Sonntag, J., Knolle, W. *J. Photochem. Photobiol. A: Chemistry* **136** (2000) 133-139; for the determination of quantum yields by conductimetry; Φ_λ = 0.5 at 308 nm, confirmed against ferrioxalate actinometer (L31*).

L36: *Sodium nitrate/ benzoic acid* in aqueous solution.

WR: 305 – 320 nm; Φ = 0.00152 ± 0.00004 (scavenging product salicylic acid), Φ = 0.00105 ± 0.00003 (formation of *p*-hydroxybenzoic acid)

AM: HPLC analysis (with absorbance and fluorescence detection) of salicylic acid and *m*/*p*-hydroxybenzoic acid or batch fluorescence (λ_{exc} = 305, λ_{em} = 410 nm) of salicylic acid (without HPLC)

PP: 10^{-2} M sodium nitrate and 10^{-3} M benzoic acid (OH radical trap) in air-saturated 2.5×10^{-3} M sodium bicarbonate solution at pH 7.2.

PP: *strong wavelength and temperature dependence,* insensitive to room lights, extremely sensitive (10^{-9} einstein still detectable)

1. 290-410 nm : Jankowski, J.J., Kleber, D.J., Mopper, K. *Photochem. Photobiol.* **70** (1999) 319-328.
2. *cf. also*: Mark, G., Korth, H.-G., Schuchmann, H.-P., von Sonntag, C. *J. Photochem. Photobiol. A: Chemistry* **101** (1996) 89-103.
3. 172 nm *cf.:* González, M.C., Braun, A.M. *Res. Chem. Intermed.* **21** (1995) 837-859.

L37: *Benzophenone/benzhydrol* photoreduction in benzene.

WR: 300 – 390 nm; relative method, no pre-determined Φ

AM: differential absorbance

1. Moore, W.M., Hammond, G.S., Foss, R.P. *J. Am. Chem. Soc.* **83** (1961) 2789-2794.
2. Moore, W.M., Ketchum, M. *J. Am. Chem. Soc.* **84** (1962) 1368-1371.
3. Murov, S.L. *Handbook of Photochemistry,* Dekker, New York 1973, p.125; 2nd ed. 1993, sect.13, p.307.
4. Borderie, B., Lavabre, D., Levy, G., Laplante, J.P., Micheau, J.C. *J. Photochem. Photobiol. A: Chemistry* **56** (1991) 13-23.

L38: *Hexan-2-one* photolysis.

WR: 313 nm; Φ = 0.22 (acetone), 0.25 (propene), 0.075 (cyclobutanol), 0.33 (2-hexanone consumed) in pentane solution

AM: GC

1. Coulson, D.R., Yang, N.C. *J. Am. Chem. Soc.* **88** (1966) 4511-4513.

2. Wagner, P.J. *Tetrahedron Lett.*, (1968) 5385-5388.

3. Murov, S.L. *Handbook of Photochemistry*, Dekker, New York 1973, p.126; 2nd ed. 1993, sect.13, p.309.

L39: *Butyrophenone* photoelimination.

WR: 313 nm; Φ = 0.24 (in benzene, ferrioxalate, L31*, used as actinometer)

AM: GC, products acetophenone and ethene

Pitts, Jr. J.N., Hess, L.D., Baum, E.J., Schuck, E.A., Wan, J.K.S., Leermakers, P.A., Vesley, G. *Photochem. Photobiol.* **4** (1965) 305-321.

L40: *Valerophenone* photolysis.

WR: 313 nm, Φ = 0.30 – 0.35 in benzene; 290-330 nm: in aqueous solution $\Phi \sim 0.98 \pm 0.04$ (cleavage plus cyclization),

$\Phi = 0.65 \pm 0.03$ (only acetophenone formation)

AM: GC, HPLC; products: acetophenone and propene, besides cyclobutanols and 1-phenylcyclopentanol

PP: no effect of pH between 4 and 7

1. Wagner, P.J., Kemppainen, A.E. *J. Am. Chem. Soc.* **94** (1972) 7495-7499.; *cf.* p.7489-7494.

2. Amrein, W., Gloor, J., Schaffner, K. *Chimia* **28** (1974) 185-188.

3. Wintgens, V., Johnston, L.J., Scaiano, J.C. *J. Am. Chem. Soc.* **110** (1988) 511-517.

4. Zepp, R.G., Gumz, M.M., Miller, W.L., Gao, H. *J. Phys. Chem. A*, **102** (1998) 5716-5723.

L41: *2-Methyl-2-phenylpropanal* photolysis.

WR: 313 nm; Φ = 0.83 in isooctane

AM: GC; products isopropylbenzene, CO, besides cyclobutanols

1. Amrein, W., Gloor, J., Schaffner, K. *Chimia* **28** (1974) 185-188.

2. H. Küntzel, H. Wolf, K. Schaffner, *Helv. Chim. Acta* **54** (1971) 868-897.

L42: *trans-2-Nitrocinnamaldehyde* photoisomerization.

WR: 313 nm, 365 nm; Φ = 0.15

AM: absorbance at 440 nm, HPLC

PP: 0.5 % methanolic solution ($A > 2$); no wavelength or temperature effect (25-40 °C); secondary products besides the *cis*-isomer upon prolonged irradiation

1. Bovina E. *et al.*, Oral commun., *2nd Intern. Meet. Photostability of Drugs*, Sept.14-16, 1997, Pavia, Italy; Albini, A. *EPA Newsletter* **61** (1997) 85-86.

2. Bovina, E., De Filippis, P., Cavrini, V., Ballardini, R. *Spec. Publ.-R. Soc. Chem.* **225** (Drugs: Photochemistry and Photostability) (1998) 305-316 - *Chem. Abstr.* **130** 43207.

L43: *Penta-1,3-diene* photoisomerization sensitized by benzophenone.

WR: 313, 366 nm; $\Phi(cis \rightarrow trans)$ = 0.55; $\Phi(trans \rightarrow cis)$ = 0.44

AM: GC

1. Murov, S.L. *Handbook of Photochemistry*, Dekker, New York 1973, p. 128; 2nd ed. 1993, sect.13, p.310.

2. Vesley, G.F. *Mol. Photochem.* **3** (1971) 193-200.

L44: *Cyclohexa-1,3-diene*, sensitized photodimerization.

WR: 313, 366 nm: Φ = 0.97 in benzene

AM: GC

Vesley, G.F., Hammond, G.S. *Mol. Photochem.* **5** (1973) 367-369.

L45*: *Fulgide* reversible photocyclization:

(E)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)succinic anhydride (Aberchrome 540) $\leftrightarrows$ 7,7a-dihydro-

2,4,7,7,7a-pentamethylbenzo[b]furan-5,6-dicarboxylic anhydride (Aberchrome 540P).

WR: 310 – 375 nm (reversible with white light); Φ = 0.20 in toluene solution (5 x 10^{-3} – 10^{-2} M); S_λ = 1640 dm^3 mol^{-1} cm^{-1} at 494 nm, 1214 dm^3 mol^{-1} cm^{-1} at 343 nm;

Φ = 0.18 (365 nm, in toluene or ethylacetate [10e]), Φ = 0.20 (365 nm, *n*-hexane [10e])

WR: back reaction 435 – 535 nm; Φ_λ = 0.073 (436 nm), 0.0594 (494 nm), 0.0470 (546 nm), linearly dependent on λ; S_λ = 487 dm^3 mol^{-1} cm^{-1} at 494 nm;

Φ = 0.09 (436 nm, in toluene [10e]), Φ = 0.06 (436 nm, in ethylacetate [10e]), Φ = 0.11 (436 nm, *n*-hexane [10e])

AM: absorbance at 494 nm (ε_{494} = 8200 dm^3 mol^{-1} cm^{-1}) or at 343 nm (ε_{343} = 6077 dm^3 mol^{-1} cm^{-1})

PP: reproducibility ± 1 %; precision ± 3 %; other solvents possible; degassing desirable while not essential; no conversion limit, but only small *A* changes necessary;

PP: while Aberchrome 540 is a widely used actinometer, there is a controversy about decreased quantum yields after repeated use [10], probably caused by side processes (*e.g.* the $E \rightarrow Z$ photoisomerization, *cf.* [6,10]); therefore, **reuse of the actinometer solution after photoreversion is strongly discouraged**; other authors [10e] see only negligible amounts of *Z* isomer and suggest other causes (ring opening), at the same time recommending a stringent recalibration.

PP: Unfortunately, Aberchrome 540 is no longer commercially available

1. Heller, H.G. *Chem. Ind.*, 193; (1978) Brit. Patent 7/1464603, USA Patent 9/719,254;

2. Heller, H.G., Langan, J.R. *J. Chem. Soc. Perkin Trans. I*, (1981) 341-343.

3. Heller, H.G., Langan, J.R. *EPA Newsletter* Oct., (1981) 71-73.

5. use in one and two-**laser** experiments: Wintgens, V., Johnston, L.J., Scaiano, J.C. *J. Am. Chem. Soc.* **110** (1988) 511-517.

6. J. Whittal, in: *Photochromism, Molecules and Systems* (Dürr, H., Bouas-Laurent, H. eds.), Elsevier, Amsterdam, 1990, Ch. 9, p.467-492.

7. quantum yields of $E \rightarrow Z$ and $Z \rightarrow E$ isomerization and *E*-cyclization and back reaction in various solvents and polymers: Yokoyama, Y., Hayata, H., Ito, H., Kurita, Y. *Bull. Chem. Soc. Jpn.* **63** (1990) 1607-1610; Deblauwe, V., Smets G., *Makromol. Chem.* **189** (1988) 2503-2512.

8. details concerning bleaching reaction: *cf.* Glaze, A.P., Heller, H.G., Whittal, J. *J. Chem. Soc. Perkin Trans. 2* (1992), 591-594; solvent effects on bleaching: Rappon, M., Syvitski, R.T. *J. Photochem. Photobiol. A: Chemistry* **94** (1996) 243-247.

9. kinetics of photodecolouration in polymer films, polystyrene, PMMA, PVA and others: Rappon, M., Chuenarm, A. Duggal, A.J., Gill, H., Bhaovibul, O., Syvitski, R.T. *Eur. Polym. J.* **27** (1991) 365-370 ; Rappon, M., Syvitski, R.T.,

Chuenarm, A. *Eur. Polym. J.* **28** (1992) 399-403.

10.   electronic substituent effects on quantum yields: Tomoda, A., Kaneko, A., Tsuboi, H., Matsushima, R. *Bull. Chem. Soc. Jpn.* **66** (1993) 330-333.

Critical discussion:

10a. Boule, P., Pilichowski, J.F. *EPA Newsletter* **47** (1993) 42-43.

10b.   reply: Heller, H.G. *EPA Newsletter* **47** (1993) 44.

10c.   Boule, P., Pilichowski, J.F. *J. Photochem. Photobiol. A: Chemistry* **71** (1993) 51-53.

10d.   photokinetics: Guo, Z., Wang, G., Tang, Y., Song, X. *J. Photochem. Photobiol. A: Chemistry* **88** (1995) 31-34.

10e.   New quantum yields: Uhlmann, E., Gauglitz, G. *J. Photochem. Photobiol. A: Chemistry.* **98** (1996) 45-49.

11.   laser actinometry*, e.g.*: Scaiano, J.C., Arnold, B.R., McGimpsey*,* W.G. *J. Phys. Chem.* **98** (1994) 5431-5434.

12.   García, C., Smith, G.A., McGimpsey, W.G., Kochevar, I.E., Redmond, R.W. *J. Am. Chem. Soc.* **117** (1995) 10871-10878.

L46: *Potassium diamminetetrakis(thiocyanato-N) chromate (potassium reineckate, K[Cr(NH₃)₂(CNS)₄])* photoaquation in dilute acidic solution. Commonly called Reinecke's salt actinometer.

WR: 316 – 750 nm: $\Phi_\lambda \sim 0.3$ dependent on λ; only slightly dependent on temperature; no significant dependence on fluence;

$S_\lambda = 30.5$ dm^3 mol^{-1} cm^{-1} at 520 nm; $\varepsilon_{520} = (110.7 \pm 2.3)$ dm^3 mol^{-1} cm^{-1}, $\varepsilon_{452} = (36.2 \pm 1.7)$ dm^3 mol^{-1} cm^{-1}, $\varepsilon_{392} = (96.3 \pm 2.5)$ dm^3 mol^{-1} cm^{-1} [4]

AM: absorbance at 450 nm of Fe(III) thiocyanate complex $\{\varepsilon = (3400 \pm 200)$ dm^3 mol^{-1} cm^{-1}[7] , **note**: *diff. from* [1]}

PP: Φ_λ = 0.291 at 316 nm, 0.388 at 350 nm, 0.335 at 366 nm, 0.316 at 392 nm, 0.310 at 416 nm, 0.311 at 452 nm, 0.299 at 504 nm, 0.286 at 520 nm, 0.282 at 545 nm, 0.270 at 577 and 585 nm, 0.276 at 600 nm, 0.271 at 676 nm, 0.284 at 713 nm, 0.302 at 735 nm, 0.273 at 750 nm [4]; thermal dark reaction; only weak red light ≥ 750 nm is admitted; the commercially available salt must be carefully recrystallized in the dark from water below 80 °C to limit thermal aquation; in basic solution thermal aquation (substitution) becomes a major problem; temperature dependence is related to pH; conversion should not exceed 10 %; reproducibility ± 2 %; precision ± 5 %;

PP: This actinometer is not recommended due to its large error and cumbersome handling

1.   Wegner, E.E., Adamson, A.W. *J. Am. Chem. Soc.* **88** (1966) 394-404.; *cf.* Searle, G.H., Bull, G.S., House, D.A. *J. Chem. Educ.* **66** (1989) 605-608.

2.   de Mayo, P., Shizuka, P. H. *Creation and Detection of the Excited State* (Ware, W.R., ed.) **4** (1976) 139-216, Dekker, New York.

3.   Demas, J.N. *Creation and Detection of the Excited State* (Ware, W.R., ed.), **4** (1976) 1-62, Dekker, New York.

4.   Hubig, S. *Diplomarbeit* (G. Gauglitz) Tübingen 1980.

5.   Szychlinski, J., Bilski, P., Martuszewski, K., Blazejowski, J. *Analyst* **114** (1989) 739-741.

6.   Görgens, E., Hänsel, R., Böttcher, H. *Experim. Techn. Physik* **35** (1987) 201-212.

7.   improved preparation of Reinecke's salt, application to biophotoreactor: Cornet, J.-F., Marty, A., Gros, J.-B. *Biotechnol. Prog.* **13** (1997) 408-415.

L47*: *9,10-Dimethylanthracene* self-sensitized photooxygenation.

WR: 334 – 395 nm; $\Phi \sim 0.6$, *cf.* table below, 1.7 x 10^{-3} M in air-saturated Freon 113 Uvasol Merck

AM: absorbance at 324 nm

λ_{irrad} /nm	$S_\lambda = \Phi_\lambda \, \varepsilon_{324}$ / dm^3 mol^{-1} cm^{-1}	standard deviation	Φ_λ	standard deviation
334	627	$\pm$ 8	0.581	$\pm$ 0.016
350	642	$\pm$ 9	0.595	$\pm$ 0.014
365	611	$\pm$ 10	0.566	$\pm$ 0.015
380	651	$\pm$ 10	0.603	$\pm$ 0.017
395	616	$\pm$ 9	0.571	$\pm$ 0.015

PP: conversion limit ~ 20 %; negligible dark reaction; independent of photon flux $10^{-7} – 10^{-9}$ einstein s^{-1}; suitable as quantum counter.

Adick, H.-J., Schmidt, R., Brauer, H.-D. *J. Photochem. Photobiol. A: Chemistry* **45** (1988) 89-96.

L48: *4-Octyl-4´-[(5-carboxypentyl)oxy]azobenzene (ABD) trans → cis* photoisomerization in an assembled monolayer film (Langmuir-Blodgett technique) coated on electrode.

WR: 334 – 405 nm; Φ_λ = 0.12 $\pm$ 0.01 (334 nm), 0.11 $\pm$ 0.01 (340 nm), 0.13 $\pm$ 0.02 (365 nm), 0.1 $\pm$ 0.05 (405 nm).

AM: *in situ* selective electrochemical reduction of *cis*-ABD; direct reading of the Faradaic charge (Coulomb meter) or the cathodic saturation current gives irradiance (after calibration against ferrioxalate, L31*).

PP: 2 x 10^{-4} M CdCl$_2$ subphase, (1.5 – 2.5) x 10^{-3} M ABD, commercially available SnO$_2$ glass (10 Ω lateral resistance) pretreated with 50 % v/v hot sulfuric acid. System several times reusable; reproducibility problems (< $\pm$ 1.7 %) with different glass substrates. Suitable for photon irradiance < 10^{-8} einstein cm^{-2} s^{-1}; irradiation times of only few seconds.

1. Liu, Z.-F., Morigaki, K., Hashimoto, K., Fujishima, A. *Anal. Chem.* **64** (1992) 134-137; *Mod. Methodol. Org. Synth., Proc. Int. Symp. Org. React. Kyoto 1991* (Shono, T., ed.), Kodansha, Tokyo, Japan, 1992, pp. 425 – *Chem. Abstr.* **123** 097468/08.
2. Morigaki, K., Liu, Z.F., Hashimoto, K., Fujishima, A. *Sensors Actuators B*, **13-14** (1993) 226-229.
3. Morigaki, K., Liu, Z.F., Hashimoto, K., Fujishima, A. *Ber. Bunsenges. Phys. Chem.* **97** (1993) 860-864.
4. Morigaki, K., Liu, Z.F., Hashimoto, K., Fujishima, A. *J. Photochem. Photobiol. A: Chemistry* **65** (1992) 285-292.

L49: *3,3,8,8-Tetramethyl-1,2.6,7-tetraazaspiro[4.4]nona-1,6-diene* photolysis in *n*-hexane.

For actinometry with circularly <u>polarized</u> light. For the determination of molar ellipticity or the degree of circularly polarized light.

WR: 345 nm

AM: CD

Blume, R., Rau, H., Schuster, O. *J. Am. Chem. Soc.* **98** (1976) 6583-6586.

L50: *1,1'-Azoxynaphthalene*.

WR: 350 nm; Φ = 0.022 at 350 nm in 95 % ethanol

AM: absorbance at $\geq$ 500 nm

PP: more pronounced spectral shift from reactant to product than with azoxybenzene (L22) but more difficult to prepare

Bunce, N.J., Debrabandere, G.G., Jacobs, K.B., Lemke, M.E., Montgomery, C.R., Nakai, J.S., Stewart, E.J. *J. Photochem.* **34** (1986) 105-115.

L51: *2,2',4,4'-Tetraisopropylazobenzene*.

WR: 350 – 390 nm; $\Phi(trans{\rightarrow}cis) = 0.112 \pm 0.04$ in heptane

AM: absorbance at 365 nm

Frank, R., Gauglitz, G. *J. Photochem.* **7** (1977) 355-357.

L52: *Riboflavin** irreversible reductive quenching by *Na$_2$EDTA* in aqueous medium in a photoelectrochemical cell.

WR: 350 – 450 nm; photocurrent depends on quencher concentration

AM: reading of photocurrent

PP: calibration against ferrioxalate, L31*, at 366, 405, 436 nm

Lingamurthy, S., Bhanumathi, V., Sethuram, B. *J. Photochem. Photobiol. A: Chemistry* **68** (1992) 395-399.

L53: *Sodium nitrite/ benzoic acid* in aqueous solution.

WR: 360 – 380 nm; $\Phi = 0.00187 \pm 0.00004$ (scavenging product salicylic acid), $\Phi = 0.00116 \pm 0.00005$ (*p*-hydroxybenzoic acid)

AM: HPLC analysis (with absorbance and fluorescence detection) of salicylic acid and *m*/*p*-hydroxybenzoic acid or batch fluorescence ($\lambda_{exc} = 305$, $\lambda_{em} = 410$ nm) of salicylic acid (without HPLC)

PP: 10^{-3} M sodium nitrite and 10^{-3} M benzoic acid (OH radical trap) in air-saturated 2.5×10^{-3} M sodium bicarbonate solution at pH 7.2;

PP: strong λ and temperature dependence; limited scavenging; insensitive to room lights, but extremely sensitive (10^{-9} einstein still detectable)

Jankowski, J.J., Kleber, D.J., Mopper, K. *Photochem. Photobiol.* **70** (1999) 319-328.

L54: *Tris(2,2'-bipyridine)ruthenium(II)** irreversible electron transfer quenching in an electrochemical cell.

WR: 360 – 580 nm; photocurrent depends on quencher and its concentration

AM: reading of photocurrent

Dressick, W.J., Meyer, T.J., Durham, B. *Isr. J. Chem.* **22** (1982) 153-157.

L55: *Tris(2,2'-bipyridine)ruthenium(II)* oxidation upon photolysis in the presence of *peroxodisulfate*.

WR: 366, 405, 436 nm; $\Phi = 1.3$ in argon-saturated aqueous solution (1.4×10^{-4} M Ru(bpy)$_3^{2+}$ and 2×10^{-3} M potassium peroxodisulfate, pH ~ 5); $S = 16600$ dm^3 mol^{-1} cm^{-1}

AM: absorbance at 450 nm

PP: Φ depends on pH and peroxodisulfate concentration; there is a slow dark reaction. Therefore, mixtures should not be stored. Absorption must be measured immediately after irradiation because of a reverse dark reaction.

1. Bolletta, F., Juris, A., Maestri, M., Sandrini, D. *Inorg. Chim. Acta* **44** (1980) L175-L176.
2. Görner, H., Kuhn, H.J., Schulte-Frohlinde, D. *EPA Newsletter* **31** (1987) 13-33.

L56: Degradation of *2,2,6,6-tetramethyl-4-oxo-1-piperidyloxyl,* or *TAN,* by photoproduced *hematoporphyrin* anion

radicals in buffered aqueous solutions. Actinometry in an EPR cavity.

WR: 366 , 405, 546 nm, $\Phi = (4.1 \pm 0.2)\ 10^{-3}$ in 0.1 M amine and borax buffer (pH 9.2), independent of λ

AM: EPR measurement of radical production

Moan, J., Hovik, B., Wold, E. *Photochem. Photobiol.* **30** (1979) 623-624.

L57*: *5,12-Diphenylnaphthacene* self-sensitized photooxygenation.

WR: 405 – 500 nm; $\Phi \sim 0.75$, *cf.* table below; in air-saturated Freon 113 Uvasol Merck (1.6×10^{-3} M);

AM: absorbance at 383 nm

λ_{irrad} /nm	$S_\lambda = \Phi_\lambda\, \varepsilon_{383} / \text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$	standard deviation	Φ_λ	standard deviation
405	666	$\pm\,12$	0.763	$\pm\,0.020$
436	662	$\pm\,11$	0.759	$\pm\,0.018$
450	670	$\pm\,12$	0.767	$\pm\,0.018$
475	671	$\pm\,12$	0.769	$\pm\,0.016$
490	657	$\pm\,13$	0.753	$\pm\,0.018$
500	644	$\pm\,13$	0.738	$\pm\,0.018$

PP: conversion limit ~ 30 %; negligible dark reaction; suitable as polychromatic quantum counter

Adick, H.-J., Schmidt, R., Brauer, H.-D. *J. Photochem. Photobiol. A: Chemistry* **45** (1988) 89-96.

L58: *p-(Diethylamino)benzenediazonium tetrafluoroborate (DEAD)* photolysis.

WR: 405 nm; $\Phi = 0.48$ in aqueous solution

AM: absorbance at about 376 nm

1. Cox, A., Kemp, T.J., Payne, D.R., Pinot de Moira, P. *J. Photogr. Sci.* **25** (1977) 208-214.
2. Baumann, H., Behrmann, K., Jahnke, H., Ortmann, W., Waldmann, G. *J. Signalaufz.-Mater.* **11** (1983) 385-394.

L59: *Thiourea* photooxidation.

WR: 420 – 660 nm; $\Phi \sim 0.98$ with ethyl chlorophyllide, $\Phi = 0.74$ with pheophytin or pheophorbid as sensitizers in pyridine

AM: O$_2$ consumption, manometric

1. Warburg, O., Schocken, V. *Arch. Biochem.* **21** (1949) 363-369.
2. Schwartz, M. *Biochim. Biophys. Acta* **22** (1956) 175-182.

L60: *4,7,7,7a-tetramethyl-2-phenyl-7,7a-dihydro-benzo[b]thiophene-5,6-dicarboxylic anhydride (Aberchrome 999P)* reversed photocyclization.

WR: 435 – 640 nm; linear dependence of Φ on λ. $\Phi_\lambda = 0.0351$ at 436 nm, 0.0240 at 546 nm, 0.0210 at 575 nm in toluene.

$S_\lambda = 288\ \text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$ at 546 nm.

AM: absorbance at 546 nm (ε_{546} = 12000 dm^3 mol^{-1} cm^{-1})

PP: reproducibility ± 0.5 %; no conversion limit; reversible (photocyclization) on exposure to 366 nm;

Reuse of the solution not recommended because some degradation takes place during recolouring.

1. private communication by Heller, H.G.

2. for similar compounds *cf.* Glaze, A.P., Harris, S.A., Heller, H.G., Johncock, W., Oliver, S.N., Strydom, P.J., Whittal, J. *J. Chem. Soc. Perkin Trans. I*, (1985) 957-961.

PP: Unfortunately, this actinometer is no longer commercially available.

L61: *Hexakis(urea)chromium(III) chloride, [Cr(urea)$_6$]Cl$_3$* photoaquation.

WR: 452 – 735 nm; $\Phi \sim 0.09 – 0.10$

AM: precipitation of the unreacted complex as the perchlorate salt and determination of chromium in the supernatant;

Wegner, E.E., Adamson, A.W. *J. Am. Chem. Soc.* **88** (1966) 394-404.

L62: *4-Dicyanomethylene-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran (DCM) trans $\rightarrow$ cis* photoisomerization.

WR: 462 nm at continuous and 532 nm at ns **laser** photolysis, Φ = 0.28 ± 0.02 (in CHCl$_3$), Φ = (2.22 ± 0.05) x 10^{-2} (in methanol)

AM: HPLC of *cis*-isomer (401 nm)

PP: strong dependence on solvent polarity; beware of light absorption by *cis*-isomer traces below 410 nm; independent of concentration; isomer equilibrium stable in the dark; no thermal reversion; insensitive to oxygen.

Mialocq, J.C., Armand, X., Marguet, S. *J. Photochem. Photobiol. A: Chemistry* **69** (1993) 351-356.

L63: *7,16-Diphenyldibenzo[a,o]perylene (meso-diphenylhelianthrene, or Actinochrome N (475/610))*
self-sensitized photooxygenation .

WR: 475 – 610 nm; Φ = 0.224 ± 0.004 in air-saturated toluene (10^{-3} M) independent of λ; S = (4080 ± 90) dm^3 mol^{-1} cm^{-1} at sea level (S = 4030, 4000, 3970 dm^3 mol^{-1} cm^{-1} at 1000, 2000, and 3000 m altitude, respectively)

AM: absorbance at 429 nm

PP: conversion limit $\sim$ 10 %; reproducibility better than ± 1 %; irreversible; no side products; suitable as polychromatic quantum counter; no dependence on λ; solutions stable at –15 °C for at most 3 months.

1. Sauvage, G. *Ann. Chim.* **2** (1947) 844-873.

2. Brauer, H.-D., Schmidt, R., Gauglitz, G., Hubig, S. *Photochem. Photobiol.* **37** (1983) 595-598.

3. Acs, A., Schmidt, R., Brauer, H.-D. *Photochem. Photobiol.* **38** (1983) 527-531.

4. Drews, W. *Dissertation* Frankfurt 1980; Hubig, S. *Dissertation* Tübingen 1984.

5. Schmidt, R., Brauer, H.-D. *J. Photochem.* **25** (1984) 489-499.

6. Schmidt, R. *Ber. Bunsenges. Phys. Chem.* **90** (1986) 813-819.

7. Adick, H.-J., Schmidt, R., Brauer, H.-D. *J. Photochem. Photobiol. A: Chemistry* **45** (1988) 89-96.

PP: Unfortunately, Actinochrome is no longer commercially available.

L64: *Cobalt(III) acidoammines* photolysis in aqueous solutions.

WR: 488 nm; $\Phi \sim 10^{-4} – 5$ x 10^{-3} at 25°C

AM: NH$_3$ release and halide aquation; absorbance at 625 nm

Pribush, R.A., Poon, C.K., Bruce, C.M., Adamson, A.W. *J. Am. Chem. Soc.* **96** (1974) 3027-3032.

L65: *7,16-Diphenyldibenzo[a,o]perylene (meso-diphenylhelianthrene, MDH)* photooxygenation sensitized by *methylene blue (MB)* .

WR: 610 – 670 nm; $A > 3$; $\Phi \sim 0.1$ in air-saturated $CHCl_3$ solution, 10^{-4} M MDH, 8 x 10^{-5} M MB; *cf.* table below (halfwidth of monochromatic light 6 nm), at 22 $\pm$ 2 °C; suitable for polychromatic radiation.

AM: change in absorbance at 405 nm of endoperoxide, $\Delta\varepsilon_{405} = \varepsilon_{405}$ (MDH) - ε_{405} (MDHPO)

λ_{irrad} /nm	$S_\lambda = \Phi_\lambda \Delta\varepsilon_{405}$ / dm^3 mol^{-1} cm^{-1}	standard deviation	Φ_λ	standard deviation
610	2062	$\pm$ 39	0.114	$\pm$ 0.003
620	1972	$\pm$ 38	0.109	$\pm$ 0.003
633 *	1918	$\pm$ 38	0.106	$\pm$ 0.003
654	1918	$\pm$ 36	0.106	$\pm$ 0.003
670	1919	$\pm$ 35	0.106	$\pm$ 0.003

* (He-Ne **laser**)

PP: contribution to initial absorbance at 405 nm by MB (0.035) and MDH (0.165); Φ independent of concentration and photon flux = 1.5 x 10^{-11} –10^{-9} einstein s^{-1}; variation of oxygen concentration has no influence; bleaching of MB is negligible.

Adick, H.-J., Schmidt, R., Brauer, H.-D. *J. Photochem. Photobiol. A: Chemistry* **49** (1989) 311-316.

L66: *7,16-Diphenyldibenzo[a,o]perylene (meso-diphenylhelianthrene, MDH)* photooxygenation. sensitized by *1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITC).*

WR: 670 – 795 nm; $\Phi \sim 0.04$, 1.6 x 10^{-4} M MDH, 7.2 x 10^{-5} M HITC in air-saturated $CHCl_3$ solution; *cf.* table below (halfwidth of monochromatic light 6 nm); suitable for polychromatic radiation.

AM: change in absorbance at 405 nm of endoperoxide, $\Delta\varepsilon_{405} = \varepsilon_{405}$ (MDH) - ε_{405} (MDHPO)

λ_{irrad} /nm	$S_\lambda = \Phi_\lambda \Delta\varepsilon_{405}$ / dm^3 mol^{-1} cm^{-1}	standard deviation	Φ_λ	standard deviation
670	818	$\pm$ 19	0.0452	$\pm$ 0.0017
680	780	$\pm$ 18	0.0431	$\pm$ 0.0017
685	769	$\pm$ 18	0.0425	$\pm$ 0.0019
695	772	18	0.0427	0.0018
700	780	17	0.0431	0.0018
705	796	17	0.0440	0.0016
710	809	17	0.0447	0.0016

720	810	17	0.0448	0.0016
730	781	16	0.0432	0.0018
745	738	15	0.0408	0.0016
755	716	15	0.0396	0.0016
770	680	15	0.0376	0.0014
780	678	14	0.0375	0.0014
795	678	14	0.0375	0.0014

PP: contribution to initial absorbance at 405 nm by MB (0.3) and HITC (0.25); Φ independent of photon flux in the range $5 \times 10^{-11} - 5 \times 10^{-10}$ einstein s^{-1}; decrease of oxygen concentration of 20 % decreases quantum yields by only 2 %; no significant dark reaction in the cold.

Adick, H.-J., Schmidt, R., Brauer, H.-D. *J. Photochem. Photobiol. A: Chemistry* **54** (1990) 27-30.

Disproved:

L67: *Decafluorobenzophenone* photoreduction in 2-propanol.

WR: 290 – 370 nm; $\Phi = 0.60 \pm 0.01$

1. Filipescu, N., Pinion, J.P., Minn, F.L. *J. Chem. Soc. Chem. Comm.* (1970) 1413.

Two independent studies advised against the use of this system because of complex stoichiometry, λ-dependent Φ, and dependence on fluence:

2. Margaretha, P., Gloor, J., Schaffner, K. *J. Chem. Soc. Chem. Comm.* (1974) 565.
3. Gauglitz, G., Kölle, U. *J. Photochem.* **4** (1975) 309-312.

II.2. Electronic Devices

Radiant power measurements before and after, or during, a photochemical reaction (the quantum yield of which is of interest) are rather cumbersome to perform with traditional methods of chemical actinometry. Integrating electronic actinometers of the "Quantacount" type [E06, 07, 10] are designed to measure and integrate the amount of light absorbed by the sample during irradiation, largely independent of the absorbance. For that purpose, the entering monochromatic light is split into a sample beam and a reference beam. By means of a chemical quantum counter (*e.g.* Rhodamine B) and photodiodes (or photoelements or photomultipliers) the two light beams produce voltages that are electrically matched. During irradiation the difference in radiant power before and behind the sample is continuously computed and converted into a frequency [E06] which is integrated, counted and displayed. The instruments allow to apply a preset amount of quanta to the sample and account for changes of the power of the light source and of the absorbance of the sample. Registration of the absorbance [E06] or taking a complete absorption spectrum [E10] are comfortable additional options allowing to monitor the photochemical conversion. The complete optical and electronic set-up has to be calibrated by chemical or physical means (see Preface) determining the einstein per count relationship for the desired wavelengths.

E01: UV light integrator as photochemical monitor.

Yip, R.W., Dickinson, D.R. *J. Sci. Instr.* **43** (1966) 758-759.

E02: Calibrated thermopile for continuous measurement of light absorption during irradiation.

Wolf, H.P., Bohning, J.J., Schnieper, P.A., Weiss, K. *Photochem. Photobiol.* **6** (1967) 321-329.

E03: Photon irradiance monitor consisting of a Rhodamin B solution and a photomultiplier.

1. Yguerabide, J. *Rev. Sci. Instr.* **39** (1968) 1048-1052.

2.   Schaarschmidt, B. *Z. Naturf.* **25b** (1970) 330-331.

E04: Physical light integrator.

Schultze, H., Vogel, H.-R. *Mol. Photochem.* **5** (1973) 223-229.

E05: Digital quantum dose integrator with memory.

Demas, J.N. *Chem. Instrumentation* **5** (1973/74) 283-290.

E06*: Electronically integrating actinometer.

WR: 254 - 578 nm (Rhodamine B as quantum counter; photoelements)

1. Amrein, W., Gloor, J., Schaffner, K. *Chimia* **28** (1974) 185-188.

2. Kuhn, H.J. *Actinometer, p. 15* in: *Instruments of Science, An Historical Encyclopedia* (Bud, R., Warner, D. eds.)
    Vol. 2, Garland Encyclopedias in the History of Science, Garland Publ. Inc., New York 1998, ISBN 0-8153-1561-9.

E07*: Electronic actinometer with photomultipliers.

 Zimmerman, H.E., Cutler, T.P., Fitzgerald, V.R., Weigt, T.J. *Mol. Photochem.* **8** (1977) 379-389.

E08: Luminescent quantum counters.

Taylor, D.G., Demas, J.N. *Analyt. Chem.* **51** (1979) 712-717; *ibid*. 717-722.

E09: $MgWO_4$ phosphor photoelectronic UV-B dosimeter for microcomputer read-out.

WR: UV-B; the emission at 420 - 560 nm is detected by a photodiode

Davidson, G., Sluder, R.B., Kofsky, I.L., Goldsmith, G. *Photochem. Photobiol.* **34** (1981) 287-296.

E10*: Integrating electronic actinometer with automatic UV/VIS monitoring.

WR: 365 – 578 nm (Rhodamine B as fluorescent converter; photodiodes)

1. Baumann, H., Behrmann, K., Jahnke, H., Ortmann, W., Waldmann, G. *J. Signalaufz.-Mater.* **11** (1983) 385-394.

2. Behrmann, K., Fanghänel, E., Kyziol, J. *Z. Chem.* **24** (1984) 20-21.

II.3. Absolute Measurement of Incident Photon Flux by Means of Photodiodes

Photodiodes are used for the detection of electromagnetic radiation in the ultraviolet, visible, and infra-red range. Their basic principle rests on the photoelectric effect. Each photon which is absorbed in the semiconductor material leads to excitation into the conduction band and produces one electron-hole-pair, which rapidly recombines in the absence

of an electric field. However, if the absorption takes place in the depletion region of the p-n junction of the diode, electrons and holes are very effectively separated by the strong local electric field. When an outside electrical connection between both sides of the junction is made, the flowing photoinduced current can be measured with high precision using an operational amplifier. Hereby, the output voltage U equals the product of photocurrent I_p and the resistance R_f of the feed-back resistor: $U = I_p \cdot R_f$.

Due to the wavelength dependence of the absorption coefficient of the semiconductor material, absorption of radiation can also occur in the layers where the separation of electrons and holes is less effective, *i.e.* before (at shorter wavelengths than the optimum one) and behind (at longer wavelengths) the p-n diffusion layer. The sensitivity of the semiconductor at a given wavelength λ is given in photocurrent (amperes) per watt of incident radiation, *i.e.*, $S_{\lambda,W}$ in A W^{-1}. In actinometry, however, it is important to have diode sensitivities related to photon flux (N_p) rather than to radiant power. $S_{\lambda,e}$ is the conversion factor transforming the photocurrent to the number of photons of wavelength λ striking the diode per unit time. With $E_\lambda = N_A \, hc/\lambda$, one einstein has the energy $E_\lambda = 0.1196/\lambda$ J for λ in m. The needed diode sensitivity $S_{\lambda,e}$ in einstein s^{-1} A^{-1} is then $S_{\lambda,e} = (S_{\lambda,W} \; E_\lambda)^{-1}$. By multiplying $S_{\lambda,e}$ by the measured photocurrent I_p the desired photon flux at the wavelength λ in einstein s^{-1} is readily obtained.

After proper calibration with an external standard, a photodiode may be used as a detector for the absolute determination of the photon flux of monochromatic radiation. Such measurements have been performed in photochemical investigations [1] and in the calibration of several chemical actinometers [2].

Precise investigations of Si photodiodes have shown that the quantum yield Φ_c of electron-hole-pair formation is actually unity for radiation of wavelengths for which absorption takes place in the p-n junction [3]. $\Phi_c = 1$ means that the charge of 96485 A s is produced by the energy $E_\lambda = 0.1196/\lambda$ J of one einstein of absorbed photons, leading to the maximum possible sensitivity $S_{\lambda,W} = 8.066 \times 10^5 \, \lambda$ A W^{-1} with λ in m. The main process reducing the sensitivity of Si photodiodes in the visible range is the reflection of the incident light at the planar surface, which amounts to about 30 % for uncoated Si. For the wavelength region where direct proportionality of $S_{\lambda,W}$ with λ holds true, the quantum yield of charge carrier formation Φ_c of the diode is constant. Photodiodes can be used as polychromatic quantum counters in this wavelength range. The determination of the quantum yield of the 1940 nm b $\rightarrow$ a emission of singlet molecular oxygen was performed with an InAs photodiode, for which Φ_c was constant from 1100 to 2700 nm according to the data sheets of the manufacturer [4].

Some mass produced Si photodiodes show direct proportionality of $S_{\lambda,W}$ with λ in a broad range of the visible spectrum, indicating a constant value of Φ_c (e. g., Hamamatsu S2387). The relative $S_{\lambda,W}$ data plotted *vs.* λ in Figure 1 have been extracted from the S2387 data sheet (URL:http://www.hamamatsu.de/assets/pdf/parts_S/S2387-1010R.pdf). Linear least squares fitting between 290 and 895 nm with fixed zero intercept results in the straight line in Figure 1. The deviation of the linear fit from the data is smaller than 12 % between 430 and 1000 nm, and even < 7 % between 450 and 1000 nm. Thus, Φ_c is in good approximation constant in this range as indicated in Figure 1. The fit follows the relation $S'_{\lambda,W} = 5.82 \times 10^5 \times \lambda$ A W^{-1}, with λ given in m. As shown above, $S_{\lambda,W} = 8.066 \times 10^5 \times \lambda$ A W^{-1} holds true in the absence of reflection loss for $\Phi_c = 1$. Therefore, the mean apparent quantum yield of charge carrier formation of the S2387 diode including reflection loss amounts to $\Phi_c = 0.72 \pm 0.05$ between 450 and 1000 nm. Thus, the charge of 72180 A s is produced by the incidence of one einstein onto the surface of the S2387 photodiode in this wavelength range resulting in the constant sensitivity $S_{\lambda,e} = 1.44 \times 10^{-5}$ einstein s^{-1}A^{-1} between 450 and 1000 nm.

Therefore, this cheap Si-photodiode may be used as a polychromatic quantum counter of constant sensitivity $S_{\lambda,e}$ = 1.44 x 10^{-5} einstein s^{-1}A^{-1} in practically the whole visible wavelength range and even in the NIR, when only moderate

accuracy is required. However, it is strongly recommended to occasionally calibrate the photodiode *vs.* a chemical actinometer or *vs.* other photodiodes of the same type, which have been kept in the dark for reference purposes.

Figure 1
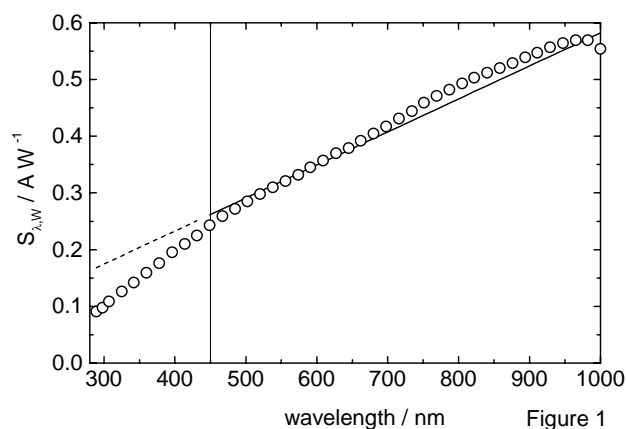
Other detectors (Si, Ge, InAs, HgCdTe) may also be used for absolute radiation measurements in the near and middle IR range, since the condition of direct proportionality of $S_{\lambda,W}$ with λ is fulfilled for several semiconductor devices [5].

References to section II.3.

1.   Photochemical set-up: Drews, W., Schmidt, R., Brauer, H.-D. *J. Photochem.* **6** (1976/77) 391-403.

2.   Calibration of chemical actinometers:
     Brauer, H.-D., Schmidt, R. *Photochem. Photobiol.* **37** (1983) 587-591.
     Acs, A., Schmidt, R., Brauer, H.-D. *Photochem. Photobiol.* **38** (1983) 527-531.

3.   Quantum yield of electron-hole-pair formation of a Si photodiode:
     Geis, J., Zalewski, E. F., Schaefer, A. R. *Appl. Opt.* **19** (1980) 3795-3799.

4.   Determination of the quantum yield of the 1940 nm b $\rightarrow$ a emission of singlet oxygen:
     Schmidt, R., Bodesheim, M. *J. Phys. Chem.* **99** (1995) 15919-15924.

5.   Spectral sensitivity of other semiconductor devices (Si, Ge, InAs, HgCdTe): Infrared Detector 1998, EG & G Optoelectronics, Judson, Laser Components GmbH, URL: http://www.lasercomponents.de

III. Standard Liquid Phase Actinometric Procedures

(For references and more data *cf.* Section II.1.3., above)

L02*: *cis-Cyclooctene cis* $\rightarrow$ *trans* photoisomerization.
(submitted by R. Srinivasan, C. von Sonntag, and H.-P. Schuchmann)
WR: 185 nm; $\Phi(cis{\rightarrow}trans)$ = 0.34; $\Phi(trans{\rightarrow}cis)$ = 0.44

A volume of 2 - 4 cm^3 of a solution of *cis*-cyclooctene in pentane (2 x 10^{-2} M, total absorption) containing nonane as a GC standard are placed in a suprasil cell and deaerated by purging with a gentle stream of oxygen-free argon while the sample is kept cold to minimize solvent evaporation. A gas-tight cell assembly is necessary. Even though

oxygen is not expected to interfere with the isomerization reaction, it may lead to relative longer wavelengths charge-transfer absorption involving the solvent. The irradiation is performed at room temperature. It is recommended to stir the solution during purging and irradiation by a Teflon-coated bar magnet. The conversion after 1 min of irradiation is easily measurable by gas chromatography at a photon flux of about 1.6×10^{16} s^{-1} (cross section 2 - 4 cm^2) at 185 nm.

This actinometer involves a system where the product, *trans*-cyclooctene, is photoisomerized back to the *cis* compound (side reactions are very minor). The number of absorbed photons per sample volume per unit time, N_p, is calculated from

$$\frac{f([cis])}{t} = - \frac{N_p}{N_A} \frac{[cis]_o}{[cis]_\infty} \, \Phi(trans \rightarrow cis)$$

where f([*cis*]) is given by the expression

$$f([cis]) = \frac{\varepsilon(cis) - \varepsilon(trans)}{\varepsilon(trans)} \, ([cis] - [cis]_o) + \left([cis]_o + \frac{\varepsilon(cis) - \varepsilon(trans)}{\varepsilon(trans)} [cis]_\infty \right) \ln \frac{[cis] - [cis]_\infty}{[cis]_o - [cis]_\infty}$$

[*cis*] is the time-dependent *cis*-cyclooctene concentration. Subscript o indicates zero conversion and ∞ refers to the stationary state ($[trans]_\infty/[cis]_\infty \sim 1$). $[cis]_\infty/[cis]_O$ is close to 0.5, $\varepsilon(cis) = 8500$ dm^3 mol^{-1} cm^{-1}, $\varepsilon(trans) = 6000$ dm^3 mol^{-1} cm^{-1}, N_A = Avogadro constant , t = irradiation time. For details and an alternative graphical method of evaluation *cf.* references in L02, Section II.1.3.

L03*: *Ethanol* photolysis (*Farkas actinometer*).
(submitted by C. von Sonntag C. and H.-P. Schuchmann)
WR: 185 nm; $\Phi(H_2) = 0.4$

2 - 4 cm^3 of a 5 M aqueous solution of pure ethanol (free of acetaldehyde and oxygen) are placed in a suprasil cell and purged with a gentle stream of oxygen-free argon while the sample is kept cold in order to minimize evaporation. A gas-tight cell assembly is necessary. Enough hydrogen is produced after one min excitation with a photon flux of about 2×10^{16} s^{-1} (cross section 2 - 4 cm^2) at 185 nm to be easily measurable by gas chromatography. Hydrogen is stripped from the sample directly into the gas chromatograph by the carrier gas. The product-collecting procedure is the same as the purging procedure. It is recommended to stir the solution during purging, irradiation, and stripping by a Teflon-coated bar magnet. As usual, the GC determination requires calibration. The hydrogen quantum yield depends on the concentration of ethanol; there is total absorption at concentrations ≥ 0.5 M.
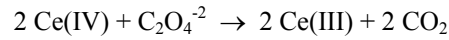

L06*: *Uranyl oxalate* photolysis.
(D.F. Eaton, O. Alfano)
WR: 200 – 500 nm; $\Phi = 0.5 - 0.6$

The chemical reaction used is the photodecomposition of oxalic acid, $H_2C_2O_4$, from a solution of uranyl oxalate.

$$H_2C_2O_4 \xrightarrow{\quad h\nu \quad} H_2O + CO_2 + CO$$
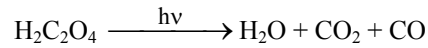
After irradiation the non-reacted $C_2O_4^{-2}$ is titrated with Ce(IV) with a solution of ceric sulfate, following the reaction:

$$2\ Ce(IV) + C_2O_4^{-2} \rightarrow 2\ Ce(III) + 2\ CO_2$$

Preparation of solutions: 0.42478 g uranyl sulfate (UO_2SO_4) and 0.67262 g disodium oxalate ($Na_2C_2O_4$, primary standard grade) are dissolved in 0.2 N H_2SO_4 and diluted to 1.0 dm^3 in the dark. The solution is 5.004 x 10^{-3} M in oxalate dianion and 1.011 x 10^{-3} M in uranyl ion. Store in the dark. Ceric sulfate is prepared from ammonium hexanitratocerate according to the procedure by Smith and Fly (L06[*], [14]), as follows. Approximately 5.5 g $(NH_4)_2Ce(NO_3)_6$ are dissolved in 15 cm^3 water and treated with 100 cm^3 15 N NH_4OH. The resulting precipitate is washed with six portions of water (25 cm^3 each) until neutral to pH paper. The precipitate is then dissolved in hot 2 N sulfuric acid (125 cm^3) and washed into a 1.0 dm^3 volumetric flask 1. The solution is cooled and brought to approximately 950 cm^3. The Ce(IV) concentration is then determined spectrophotometrically by dilution of an aliquot and measurement of the absorbance at 320.0 nm *vs.* 0.2 N H_2SO_4 in a 1.0 cm cell. The decadic molar absorption coefficient of Ce(IV) at 320 nm is ε_{320} = 5.41 x 10^3 $dm^3\,mol^{-1}\,cm^{-1}$. The concentration of Ce(IV) is then adjusted until it is slightly larger than twice the (molar) concentration of oxalate in the actinometer solution.

PP: The use of commercial ceric sulfate is not recommended, since it is contaminated by ammonium nitrate which limits the stability of standardized cerium solutions.

Procedure: After irradiation of two 3.0 cm^3 aliquots of actinometer solution, a 1.0 cm^3 aliquot is pipetted into a 10.0 cm^3 volumetric <u>flask 2</u>. 1.0 cm^3 of the standard Ce(IV) solution and 1.0 cm^3 H_2SO_4 (2 N) are added and the solution brought to the mark with water. Both irradiated samples and non-irradiated blanks are treated in this way. The solutions are then incubated at 80 °C for 10 min and allowed to cool in the dark.

Calculations: The photon flux N_p/einstein s^{-1} entering the sample cell is given by:

$$N_p = \frac{V_{irrad}\ \Delta A\ V_{flask2}}{2\ t\ \varPhi\ f\ l\ \varepsilon_{320}\ V_{aliq}}$$

with V_{irrad} = volume of irradiated actinometer solution (recommended 3 cm^3); V_{flask2} = volume of the reaction flask 2 (recommended 0.01 dm^3), V_{aliq} = volume of the measured aliquot (recommended 1 cm^3), t = time of irradiation; $\varPhi$ = quantum yield of oxalate loss; f = fraction of incident actinometric light absorbed by actinometer solution (0.999; this factor depends on irradiation wavelength and pathlength); ε_{320} = molar absorption coefficient of cerium(IV) at 320.0 nm. The factor 2 in the denominator results from the stoichiometric factor in the titration reaction. The absorbance difference between sample and non-irradiated blank (ΔA) is determined at 320.0 nm (l = pathlength, usually 1 cm).

The oxalate photodecomposition quantum yields ($\varPhi_\lambda$) are:

λ /nm	Φ_λ	λ /nm	Φ_λ	λ /nm	Φ_λ
208	0.48	254	0.60	335	0.53
237	0.58#	265	0.58	366	0.49
243	0.60#	278	0.58	405	0.56
245	0.61	302	0.57	436	0.58
248	0.61#	313	0.56		

The marked (#) values in the table are interpolations from the other data (after Leighton and Forbes [1], and Brackett and Forbes [2], L06*).

Comments: The procedure discussed here is an improved version of one due to Pitts. The sensitivity of the method is only half of that of the conventional ferrioxalate procedure (L31*, largely because ε of Ce(IV) at the analysing wavelength is only half that of the phenanthroline-Fe(II) complex used in the analysis during the ferrioxalate procedure). The success of this method also depends critically on the concentration of Ce(IV): if the concentration is less than that required to oxidize all the oxalate in the non-irradiated blank, the results will be meaningless; if the concentration is significantly greater than twice the oxalate concentration of the blank then the absorbances measured for the blank and irradiated samples will be so large as to render invalid differential absorption techniques. Considerable care must be exercised when using the uranyl oxalate actinometer, and one should always check the integrity of freshly prepared solutions by comparing photon flux measured by uranyl oxalate actinometry to that obtained using ferrioxalate actinometry at a wavelength at which quantum yields are known for both systems.

The uranyl may be recovered as sulfate. For this purpose the used actinometric solutions are collected and photolyzed until complete oxidation of the oxalate. The photolyzed solution is then concentrated under vacuum and the sulfate may be crystallized and recrystallized after adding sulfuric acid.

PP: *Take care to dispose of the uranium waste in accordance with the current legal regulations.*

L11*: *Azobenzene [Actinochrome 2R (245/440)]* photoisomerization (reusable).
(submitted by G. Gauglitz)
WR: 230 – 460 nm; $\Phi(trans{\rightarrow}cis) = 0.14$; $\Phi(cis{\rightarrow}trans) = 0.48$; $S = 130 – 3900\ mol^{-1}\ dm^3\ cm^{-1}$

Wavelength range 245-266 nm: The solution is pre-irradiated at 313 nm. The actinometry (as above) then starts at the photostationary state ($A_{358} \sim 0.30$) and the final value should be $A_{358} < 0.45$.

Wavelength range 270-340 nm: The absorbance A of a 6.4×10^{-4} M methanol solution of azobenzene, stored in the dark (see below), is measured at 358 nm. A value of $A_{358}\ ca.1$ is recommended. Each irradiation period should cause a change in A_{358} of about 0.02 and the final value should be kept between 0.85 and 0.9. Except during irradiation, only radiation ≥ 500 nm is to be admitted to the sample. For regeneration a sealed cell should be stored in the dark or irradiated at 254 nm.

Wavelength range 350 – 440 nm: There is *no total absorption* in this range. Irradiation and observation wavelengths should be the same. For the range 375 – 440 nm, a pre-irradiated solution is used and the procedure starts at the photostationary state. Efficient stirring of the solution is essential in all cases.

Evaluation: For the *range 245-340 nm* the following formula is used, where ΔA_{358} is the change in absorbance at

358 nm and t is the irradiation time in seconds. The factors F_λ are given in the table below. Thus, the photon irradiance, E_P, entering the sample cell is given by $E_P = F_\lambda \cdot \Delta A_{358} / t$ in einstein cm^{-2} s^{-1}.

λ_{irrad}/nm	F_λ / einstein cm^{-2}
245	$2.30 \cdot 10^{-6}$
280	$4.60 \cdot 10^{-6}$
302	$4.63 \cdot 10^{-6}$
313	$5.30 \cdot 10^{-6}$
334	$3.60 \cdot 10^{-6}$

The ratios of the irradiated volumes as well as of the front areas of actinometric and reaction cell have to be taken into consideration in case the photon flux (einstein s^{-1}) is desired. Ideally, the photoreaction should be made in a cuvette of the same dimensions as that used for the actinometer.

For the *range 350 – 440 nm* graphical or arithmetical kinetic evaluation methods have to be used (*cf.* L11* [2,3]). The latter is done with the aid of a computer. The graphical method uses the expression $E_P = \dfrac{\tau}{\mathbf{Q} \times t}$, where $\mathbf{Q} =$

[Φ(*trans→cis*) · ε(*trans*) + Φ(*cis→trans*) · ε(*cis*)] 1000, is the *pseudo total quantum yield*, with ε at the irradiation wavelength. $\mathbf{Q}$ values are independent of time and concentration. They are listed in the literature, but should be determined for each lamp/filter combination at the irradiation wavelengths. τ is taken from calibration graphs of the time-dependent absorbance *vs.* t.

L31*: *Potassium tris(oxalato)ferrate(III) (potassium iron(III) oxalate*, K$_3$[Fe(C$_2$O$_4$)$_3$]·3H$_2$O*), photoreduction (*Hatchard-Parker actinometer, commonly called ferrioxalate actinometer*).
(Submitted by G. Gauglitz and S. Hubig)
WR: 250 – 500 nm; Φ = 1.25 – 0.9; S = 13900 – 9990 dm^3 mol^{-1} cm^{-1}

All procedures should be done under red safe-light. Green crystals of K$_3$[Fe(C$_2$O$_4$)$_3$]·3H$_2$O are prepared by mixing 3 vol. 1.5 M K$_2$C$_2$O$_4$ with 1 vol. 1 M FeCl$_3$ solution, recrystallized three times from warm water, dried at 45 °C and kept in the dark. 0.006, 0.012, or 0.15 M ($\geq$ 405 nm) solutions can be used for actinometry. A 0.006 M solution is prepared by dissolving 2.947 g of the crystals in 100 cm^3 H$_2$SO$_4$ (1 N) and dilution with distilled water to 1 dm^3. An absorption spectrum of the solution is taken. Total absorption at the desired irradiation λ and optical pathlength is recommended. *E.g.*, 3 cm^3 (V_1) of the solution are irradiated under efficient stirring. 1 cm^3 (V_2) of the irradiated solution is given into a 10 cm^3 (V_3) volumetric flask containing a mixture of 4 cm^3 0.1 % 1.10-phenanthroline solution (store in the dark !) and 0.5 cm^3 buffer (stock solution: 82 g NaC$_2$H$_5$CO$_2$, 10 cm^3 conc. H$_2$SO$_4$, diluted to 1 dm^3 with distilled water) which is then diluted to the mark with distilled water. It is essential that the irradiation time measurement (electronic shutter) as well as the pipetting is done very precisely. A reference is prepared in the same way except that it has not been irradiated. Both solutions are kept in the dark (about an hour) until full colour development is achieved, and the absorbance difference between the two samples is measured at 510 nm (1 cm optical pathlength (l), ε_{510} = 11100 dm^3 mol^{-1} cm^{-1}). A_{510} should be within the range 0.4 – 1.8. Conversion should not exceed 5 %. The photon flux, N_p, in einstein s^{-1}

entering the sample cell is given by:

$$N_P = \frac{\Delta A \quad V_1 \quad 10^{-3} \quad V_3}{\Phi_\lambda \quad \varepsilon_{510} \quad V_2 \quad l \quad t}$$

where t is in seconds. At room temperature $\Phi_\lambda = 1.20 - 1.26$ (0.006 M) for the wavelength range 254 – 366 nm, $\Phi_\lambda = 1.14$ at 405 nm, 1.11 (0.006 M) at 436 nm, 1.12 (0.01 M) at 458 nm, 1.08 (0.08 M) at 488 nm, and 0.93 (0.20 M) at 514 nm. There is no total absorption above 450 nm even in 0.15 M solution. In this case the value of the photon flux must be divided by the fraction of absorbed light at the irradiation wavelength, $(1-10^{-A})$. The procedure described in *Murov's Handbook of Photochemistry* (L31*[12]) is also recommended, but the precautions listed above should be obeyed.

PP: due to its high S-value L31* is not really an integrative system, *i.e.* periodical fluctuations in radiation power may not be "seen" during the rather short irradiation periods.

L45*: *Fulgide* reversible photocyclization:

(E)-[1-(2.5-dimethyl-3-furyl)ethylidene](isopropylidene)succinic anhydride (Aberchrome 540) $\leftrightarrows$ 7.7a-dihydro-

2.4.7.7.7a-pentamethylbenzo[b]furan -5.6-dicarboxylic anhydride (Aberchrome 540P).

(submitted by H.G. Heller)

WR: 310 – 375 nm; $\Phi = 0.2$; $S = 1640$ dm^3 mol^{-1} cm^{-1}

A *ca.* 5 x 10^{-3} M solution is prepared by dissolving 25 mg Aberchrome 540 in 20 cm^3 toluene. An accurately measured volume (*e.g.* 3 cm^3) of this solution is pipetted into a cuvette and the absorbance (if any) at 494 nm is noted. The stirred solution is then irradiated for a known period. A magnetic stirrer is recommended. Care should be taken to prevent the magnetic stirrer from entering the light beam. It is essential that the solution absorbs all radiation falling upon it. After irradiation in a 1 cm cell (l) and mixing, the absorbance at 494 nm is measured. The increase in absorbance (ΔA_{494}) enables the photon flux, N_p in einstein s^{-1}, entering the sample cell, to be calculated from

$$N_P = \frac{\Delta A \quad V}{\Phi \quad \varepsilon_{494} \quad l \quad t}$$

where V = irradiated volume in dm^3, $\Phi = 0.20$ from 310 - 375 nm, $\varepsilon_{494} = 8200$ dm^3 mol^{-1} cm^{-1},

t = time in seconds. For recent quantum yields *cf.* [10e]. The coloured form is reversed with white light;

PP: *Re-use of the actinometer solution after photoreversion is strongly discouraged*).

Unfortunately, Aberchrome 540 is no longer commercially available.

L47*: *9,10-Dimethylanthracene self-sensitized photooxygenation.*

(submitted by R. Schmidt)

WR: 334 – 395 nm; $\Phi = 0.583 \pm 0.15$; $S = (629 \pm 17)$ dm^3 mol^{-1} cm^{-1}

A defined volume of a 1.7×10^{-3} M solution of 9,10-dimethylanthracene in air-saturated Freon 113 (molar absorption coefficient $\varepsilon_{324} = 1080$ mol^{-1} dm^3 cm^{-1}) of initial absorbance $A_{324} = 1.8$ (optical pathlength $l = 1$ cm) is filled into a

spectrophotometric cell equipped with a magnetic stirring bar. Radiation of $\lambda < 435$ nm should be completely avoided during preparation and handling of the solution. The solution completely absorbs the incident radiation in the wavelength range 334 – 395 nm. During irradiation stirring is essential. The photon flux, N_p (in einstein s^{-1}) entering the sample cell is calculated by using the absolute value of the absorbance decrease at 324 nm upon irradiation (ΔA_{324}) and the following equation

$$N_P = \frac{\Delta A_{324} \; V}{\varepsilon_{324} \; \Phi \; t \; l}$$

with t = irradiation time in seconds, V = volume of the solution in dm^3 (density = 1.575 g cm^{-3}). The conversion should not exceed 20 %. The system is suited as a polychromatic quantum counter independent of wavelength with $\varepsilon_{324} \cdot \Phi$ = (629 ± 17) dm^3 mol^{-1} cm^{-1} and $\Phi = 0.583 \pm 0.015$. Values of $S = \varepsilon_{324} \cdot \Phi$ at particular irradiation wavelengths are given under L47* in section II.1.3.

L57*: *5,12-Diphenylnaphthacene* self-sensitized photooxygenation.
(submitted by R. Schmidt)
WR: 405 – 500 nm; $\Phi = 0.758 \pm 0.16$; $S = (662 \pm 13)$ dm^3 mol^{-1} cm^{-1}

A defined volume of a 1.6×10^{-3} M solution of 5,12-diphenylnaphthacene in air-saturated Freon 113 (molar absorption coefficient $\varepsilon_{383} = 873$ dm^3 mol^{-1} cm^{-1}) of initial absorbance $A_{383} = 1.4$ (optical pathlength $l = 1$ cm) is filled into a spectrophotometric cell equipped with a magnetic stirring bar. Only yellow or red light ≥ 560 nm may be used during preparation and handling of the solution. The solution completely absorbs the incident radiation in the useful wavelength range 405 – 520 nm. During irradiation stirring is essential. The photon flux, N_p (einstein s^{-1}) entering the sample cell is calculated by using the absolute value of the absorbance decrease at 383 nm upon irradiation (ΔA_{383}) and the following equation

$$N_P = \frac{\Delta A_{383} \; V}{\varepsilon_{383} \; \Phi \; t \; l}$$

with t = irradiation time in seconds, V = volume of the solution in dm^3 (density = 1.575 g cm^{-3}). The conversion should not exceed 30 %. The system is suited as a polychromatic quantum counter independent of wavelength with $S = \varepsilon_{383} \cdot \Phi$ = (662 ± 13) dm^3 mol^{-1} cm^{-1} and $\Phi = 0.758 \pm 0.016$. Values of $S = \varepsilon_{383} \cdot \Phi$ at particular rradiation wavelengths are given under L57* in section II.1.3.

Appendix

Additional references concerning practical problems as well as kinetic and theoretical aspects of quantum yield calculation:

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