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SUBCOMMITTEE ON PHOTOCHEMISTRY**

CHEMICAL ACTINOMETRY

(IUPAC Technical Report)

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Chemical actinometry

(IUPAC Technical Report)

Abstract: This document updates the first version of the IUPAC technical report on "Chemical actinometers" published in *Pure Appl. Chem.* **61**, 187–210 (1989). Since then, some methods have been improved, procedures have been modified, and new substances have been proposed as chemical actinometers. An actinometer is a chemical system or a physical device by which the number of photons in a beam absorbed *into* the defined space of a chemical reactor can be determined integrally or per time. This compilation includes chemical actinometers for the gas, solid, microheterogeneous, and liquid phases, as well as for the use with pulsed lasers for the measurement of transient absorbances, including the quantum yield of phototransformation, as well as the literature for each of the actinometers. The actinometers listed are for the use in the wavelength range from the UV to the red region of the spectrum. A set of recommended standard procedures is also given. Advantages and disadvantages are discussed regarding the use of chemical actinometers vs. electronic devices for the measurement of the number of photons absorbed. Procedures for the absolute measurement of incident photon flux by means of photodiodes are also discussed.

CONTENTS

ABBREVIATIONS

AM	analytical method
CA	chemical actinometer
E	electronic device
G	gas phase
GC	gas chromatography
HPLC	high-pressure liquid chromatography
IR	infrared
L	liquid phase
LC	liquid chromatography
PP	procedure, precautions, comments
S	solid phase
WR	wavelength range

QUANTITIES, SYMBOLS, AND UNITS

Name	Symbol	Definition	SI units	Notes
absorbance (decadic)	A, A_{10}	$A = \lg(P^0/P) = -\lg T$	1	1
absorption coefficient				
linear decadic	a	$a = A_{10}/l$	m^{-1}	2
molar decadic	ε	$\varepsilon = a/c = A_{10}/cl$	$m^2\ mol^{-1}$	3
absorption cross-section	σ	$\sigma = (\varepsilon/N_A)\ln 10$	m^2	4
actinometric factor		See *sensitivity*		
amount of photons	n_p		mol	5
amount concentration	c	$c = n/V$	$mol\ m^{-3}$	6
area	S		m^2	
Avogadro constant	N_A	$N_A = 6.022\ 141\ 5 \times 10^{23}\ mol^{-1}$	mol^{-1}	7
electric current	i		A	
fluence	H'	$H' = \int E'\ dt$	$J\ m^{-2}$	8
frequency (linear)	ν	$\nu = c/\lambda$	Hz	
irradiance, intensity (radiant flux received)	E	$E = dP/dS$	$W\ m^{-2}$	
lifetime	τ	$c(t = \tau) = c(t = 0)/e$	s	
optical pathlength	l		m	
photon fluence	H_p'	$H_p' = dN_p/dS$	m^{-2}	9
photon fluence rate	E_p'	$E_p' = dH_p/dt$	$m^{-2}\ s^{-1}$	9
photon flux, amount basis	$q_{n,p}$	$q_{n,p} = q_p/N_A$	$mol\ s^{-1}$	10
photon flux, number basis	q_p	dN_p/dt	s^{-1}	9, 11
photon irradiance	E_p	$E_p = dq_p/dS$	$m^{-2}\ s^{-1}$	9, 12
photon number	N_p	$N_p = n_p\ N_A$	1	
pressure	p		Pa	
quantum yield	Φ	Φ = (number of events)/ (number of photons absorbed)	1	
of charge carrier formation in a photodiode	Φ_c			
radiant energy	Q	$\int_\lambda Q_\lambda\ d\lambda$	J	
radiant exposure		See *fluence*		
radiant intensity	I	$I = dP/d\Omega$	$W\ sr^{-1}$	
radiant power, radiant energy per time	P	$P = dQ/dt$	W	13

(*continues on next page*)

Table (*Continued*).

Name	Symbol	Definition	SI units	Notes
radiative lifetime	τ_0	$\tau_0 = 1/k_r$	s	
rate constant for radiative step	k_r		s^{-1}	
refractive index	n	$n = c_0/c$	1	
sensitivity				
of an actinometer	S_{ac}	$S_{ac}(\lambda) = \Phi(\lambda)\ \varepsilon(\lambda_{obs})$ or $S_{ac}(\lambda) = \Phi(\lambda)\ \Delta\varepsilon\ (\lambda_{obs})$	$m^2\ mol^{-1}$	14
of a photodiode	S_{pd}	$S_{pd} = I_{pd}/P$	$A\ W^{-1}$ $= V^{-1}$	15
solid angle	Ω	$\Omega = S/r^2$	sr, 1	16
spectral fluence (in terms of wavelength)	H'_λ	$H'_\lambda = dH'/d\lambda$	$J\ m^{-3}$	17
speed of light				
in vacuum	c_0	$c_0 = 299\ 792\ 458\ m\ s^{-1}$	$m\ s^{-1}$	
in a medium	c	$c = c_0/n$	$m\ s^{-1}$	
temperature, Celsius	θ	$\theta/°C = T/K - 273.15$	°C	
temperature, thermodynamic	T		K	
time	t		s	
transmittance	T	$T = P/P^0$	1	1
volume	V		m^3	
wavelength	λ		m	
wavenumber	$\tilde{\nu}$	$\tilde{\nu} = \nu/c_0 = 1/n\ \lambda$	m^{-1}	

Notes

1. If losses from reflection, scattering, and luminescence are neglected, $T = P/P^0 = I/I^0$, where superscript 0 indicates incident radiant energy and no superscript transmitted radiant energy.
2. In spectroscopy, usually defined in terms of the spectral radiant power, $P_\lambda = dP(\lambda)/d\lambda$.
3. Numerical values are often quoted in $mol^{-1}\ dm^3\ cm^{-1}$. Note the lack of compactness in using two submultiples of length.
4. In spectroscopy, the net cross-section resulting from the sum of effects due to absorption and induced emission. A conversion equation in common units is $\sigma/cm^2 = (3.823\ 6 \times 10^{-21}/mol) \times (\varepsilon/dm^3\ cm^{-1}\ mol^{-1})$.
5. Amount of photons is often given in the non-SI unit einstein = mol.
6. The usual units are $mol\ dm^{-3}$ or $mol\ l^{-1}$ or submultiples. Commonly, the non-SI unit M (small cap) is used as an abbreviation for $mol\ dm^{-3}$.
7. 2002 value [1].
8. For a parallel and normally incident beam, a synonym is *radiant exposure*. When applied to the total radiant energy incident from all directions, the symbol H' is used.
9. These quantities, defined on a number basis, can be expressed on a chemical amount basis by dividing by the Avogadro constant, e.g., photon flux (chemical amount basis) = q_p/N_A. If distinction needs to be made between quantities based on chemical amount and number, then symbols such as $q_{n,p}$ and q_p can be used.
10. A common unit is einstein s^{-1}. A term not in accordance with the usual definition of flux [2].
11. As defined in [4] (see also [5]); called *photon flux* in [3], a term not in accordance with the usual definition of flux [2].
12. Equivalent to photon fluence rate for a parallel beam not scattered or reflected.
13. Definition from [2]; synonymous with *radiant energy power, radiant energy flux* defined in [3].
14. λ is the excitation wavelength, and λ_{obs} is the observation wavelength which may be the same as or differ from the former. The first definition corresponds to the case in which the actinometer does not absorb at λ_{obs}, whereas the second definition corresponds to the case in which the actinometer absorbs at λ_{obs}. Common units are $dm^3\ mol^{-1}\ cm^{-1}$.
15. Related to $q_{n,p}$ by $q_{n,p} = [\lambda/(N_A\ h\ c\ S_{pd})]\ i_{pd}$ with i_{pd} the electric current of the photodiode.
16. The stearadian is an SI supplementary unit, but is dimensionless, so has SI unit 1.

17. Other physical quantities X such as irradiance, photon flux, photon fluence, photon fluence rate, and radiant intensity may be used to derive the corresponding "spectral" quantity (relative to wavelength) by $X_\lambda = \mathrm{d}X/\mathrm{d}\lambda$. Analogous quantities relative to frequency or to wavenumber may also be defined.

Entries in the table are consistent with terminology, symbols, and units given in [2,3], and are slightly modified from those in [4], terms from which are included in [5].

References for Table 1:

1. <http://physics.nist.gov/constants>
2. IUPAC. *Quantities, Units and Symbols in Physical Chemistry* (the 'Green Book'), 2nd ed., prepared for publication by I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu, Blackwell Science, Oxford, UK (1993).
3. ISO 31–6:1992(E), *Handbook on Quantities and Units, Part 6: Light and related electromagnetic radiations*, ISO, Geneva, Switzerland (1992).
4. IUPAC Organic Chemistry Division, Commission on Photochemistry. *Glossary of Terms Used in Photochemistry* (2nd ed.), prepared for publication by S. E. Braslavsky, K. N. Houk (1st ed.), J. W. Verhoeven (2nd ed.). *Pure Appl. Chem.* **60**, 1055 (1996).
5. IUPAC. *Compendium of Chemical Terminology, IUPAC Recommendations*, 2nd ed., compiled by A. D. McNaught and A. Wilkinson, Blackwell Science, Oxford, UK (1997).

PREFACE

The first version of this document appeared in *Pure Appl. Chem.* **61**, 187–210 (1989). Since then, some methods have been improved, and some procedures have been modified. The Photochemistry Commission (1998–2001) and subsequently the Subcommittee 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 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, see below), an actinometer is a chemical system or a physical device by which the number of photons in a beam absorbed *into* the defined space of a chemical reactor can be determined integrally or per time.

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, $\Phi(\lambda)$, is accurately known. Measuring the reaction rate allows the calculation of the absorbed photon flux. The incident photon flux $q_\mathrm{p}{}^\mathrm{o}$ is calculated from the relation $q_\mathrm{p}(\mathrm{abs}, \lambda) = q_\mathrm{p}{}^\mathrm{o}(\lambda)\ (1-10^{-A(\lambda)})$, provided that the decadic absorbance $A(\lambda)$ is constant ±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 $q_\mathrm{p}(\mathrm{abs}, \lambda) = q^\mathrm{o}(\lambda)$ 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/W m^{-2} or photon irradiance, E_p/s^{-1} m^{-2} or $E_{n,p}$/einstein s^{-1} m^{-2} or photon flux, $q_{n,p}$/einstein s^{-1}, using precalibrated photodiodes is described in Section 2.3 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 1 of this document and consult, e.g.,

- A. M. Braun, M.-T. Maurette, E. Oliveros. *Photochemical Technology*, John Wiley, New York (1991); idem*, Technologie Photochimique,* Presses Polytechniques Romandes, Lausanne (1986); *CRC Handbook of Organic Photochemistry*, J. C. Scaiano (Ed.), 2 vols., CRC Press, Boca Raton (1989).
- S. L. Murov, I. Carmichael, G. L. Hug. *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, New York (1993).

For the most recent version of "Glossary of terms and definitions used in photochemistry", refer to:

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

1. GENERAL CONSIDERATIONS ON CHEMICAL ACTINOMETRY

1.1 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 for about 70 years in photochemistry as a relatively simple and accurate method for radiation measurement [2].

Owing 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 silicon 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.

1.2 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. **Reading the original literature on each actinometer prior to its use is highly recommended.**

1.3 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 that have been investigated especially at high photon fluxes using laser excitation can be used as standards for this purpose [7].

1.4 Potential errors in chemical actinometry

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

1.4.1 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 flux, number basis, $q_\mathrm{p}/\mathrm{s}^{-1}$, or photon flux, amount basis, $q_{n,\mathrm{p}}/\mathrm{einstein\ s}^{-1}$, 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., $P_b = P/(1 - R)$.

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 [2,2,2–trifluoroethan-1-ol] ($n = 1.29$), to 0.959 for toluene ($n = 1.49$), and to 0.956 for CS_2 ($n = 1.63$). At 400 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 nonpolarized 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° [8].

1.4.2 Temperature

The influence of temperature variation has been investigated for only 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.

1.4.3 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, 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.

1.4.4 Degree of absorption by the chemical actinometer

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 unfavorable 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].

1.4.5 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 1:

1. J. W. Verhoeven. *Pure Appl. Chem.* **68**, 2223–2286 (1996).
2. W. G. Leighton and G. S. Forbes. *J. Am. Chem. Soc.* **52**, 3139–3152 (1930).
3. K. Bischoff. *Optik* **28**, 183–189 (1968/69).
4. R. J. Phelan, Jr. and A. R. Cook. *Appl. Opt.* **12**, 2494–2500 (1973).
5. J. Geist and W. R. Blevin. *Appl. Opt.* **12**, 2532–2535 (1973).
6. J. L. Gardner and F. J. Wilkinson. *Appl. Opt.* **24**, 1531–1534 (1985).
7. J. N. Demas, W. D. Bowman, E. F. Zalewski, R. A. Velapoldi. *J. Phys. Chem.* **85**, 2766–2771 (1981).
8. B. M. Jaworski and A. A. Detlaf. *Physik griffbereit*, p. 567, Vieweg und Sohn, Braunschweig (1972).

2. 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.**

Note carefully that names of chemicals are given usually as common names that appear in the relevant publications. Systematic IUPAC names are given in square brackets where applicable.

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

2.1 Chemical systems

Several physical methods for the calibration of light sources (see Sections 1, 2.2, and 2.3) 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 1.4.1). A recommended alternative, especially for low photon densities at which multiphoton processes do not play a role, is to use a totally absorbing actinometer solution (see Section 1.4.4).

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

2.1.1 Solid- and microheterogeneous-phase chemical actinometers

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

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

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. G. J. Fisher and H. Johns. In *Photochemistry and Photobiology of Nucleic Acids*, Vol. 1, S. Y. Wang (Ed.), Chap. 5, pp. 225–294, Academic Press, New York (1976).
2. P. Grof, S. Gaspar, G. Rontó. *Photochem. Photobiol.* **64**, 800–806 (1996).

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. Y. Ishigaki, A. Takayama, S. Yamashita, O. Nikaido. *J. Photochem. Photobiol., B* **50**, 184–188 (1999), and refs. therein; some related “living dosimeters”:
2. Biofilm of *Bacilus subtilis* spores, L. E. Quintern, G. Horneck, U. Eschweiler, H. Bücker. *Photochem. Photobiol.* **55**, 389–395 (1992).
3. Special *Escherichia coli* bacteria strain K12 AB2480 (uvrA$^-$ recA$^-$) with photodamage repair deficiency (193, 254 nm), G. G. Gurzadyan, H. Görner, D. Schulte–Frohlinde. *Rad. Research* **141**, 244–251 (1995) and refs. therein, especially by P. Howard-Flanders et al.
4. cf., e.g., Special issue on biological dosimetry of UV radiation, A. Fekete and G. Rontó (Eds.). *J. Photochem. Photobiol., B* **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. T. J. Tate, B. L. Diffey, A. Davis. *Photochem. Photobiol.* **31**, 27–30 (1980).
2. N. K. Gibbs and A. R. Young. *Photochem. Photobiol.* **37**, 345–348 (1983).

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_2O] ratio
A TiO_2-sol-based actinometer used to determine number of photons absorbed
AM: decrease of thymine absorption at 265 nm

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

S05: Azoxybenzene → 2-hydroxyazobenzene, cf. **L22**
WR: 300–400 nm; poly(methyl methacrylate) block; $\Phi \sim 10^{-3}$
AM: absorbance at 420 nm

1. N. J. Bunce and J. J. Smith. *J. Photochem.* **23**, 219–231 (1983).
2. N. J. Bunce, G. G. Debrabandere, K. B. Jacobs, M. E. Lemke, C. R. Montgomery, J. S. Nakai, E. J. Stewart. *J. Photochem.* **34**, 105–115 (1986).

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. J. N. Pitts, Jr., J. K. S. Wan, E. A. Schuck. *J. Am. Chem. Soc.* **86**, 3606–3610 (1964).
2. J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, G. Vesley. *Photochem. Photobiol.* **4**, 305–321 (1965).
3. G. W. Cowell and J. N. Pitts, Jr. *J. Am. Chem. Soc.* **90**, 1106–1110 (1968).
4. P. Leighton and F. A. Lucy. *J. Chem. Phys.* **2**, 756–759 (1934).
5. C. B. Roy and S. C. Das. *Ind. J. Chem.* **14A**, 653–655 (1976).
6. E. M. Fleischmann. *Limnol. Oceanogr.* **34**, 1623–1629 (1989); 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., J. M. Allen, S. A. Allen, J. Dreiman, S. W. Baertschi. *Photochem. Photobiol.* **69**, 17S–18S (1999).

S07: Polysulfone UV-B film dosimeter
WR: ≤315 nm
AM: absorbance change at 300 nm

1. A. Davis, B. L. Diffey, T. K. Tate. *Photochem. Photobiol.* **34**, 283–286 (1981); ΔA(300 nm) mathematically correlates with the UV (300 nm) radiant exposure H/J m^{-2}. Irradiance was measured using a vacuum thermopile.
2. B. L. Diffey. *Photochem. Photobiol.* **46**, 55–60 (1987); Quantitative erythemal effectiveness given vs. λ; comparison of radiometric with actinometric measurements.
3. Some related UV-A and B dosimeter systems: polycarbonate plastic, C. F. Wong, R. Fleming, S. J. Carter. *Photochem. Photobiol.* **50**, 611–615 (1989).
4. Fuchsin and sandolan yellow dyes in polyvinyl alcohol polymer, F. A. Rehim, A. S. A. Gawad, A. A. A. Fattah. *J. Photochem. Photobiol., A* **64**, 123–131 (1992).

S08: Diels–Alder adduct of 2,5-dimethylbenzoquinone and cyclopentadiene [4a,7-dimethyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione] 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

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

S09: Quinonaphthalone [2-(2-quinolyl)indane-1,3-dione] photofading
Plastic plates
WR: 366–436 nm; $\Phi = 2 \times 10^{-5}$
AM: absorbance decrease at 420 nm

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

2.1.2 Gas-phase chemical actinometers

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

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

G02: Nitrogen monoxide (NO) photoionization
WR: ≤134 nm, $\Phi(\lambda$, 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. K. Watanabe, F. M. Matsunaga, H. Sakai. *Appl. Opt.* **5**, 391–396 (1967).
2. J. Bercowitz. *Physics Essays* **13**, 248–255 (2000).

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

G03*: Dinitrogen oxide (N_2O) photolysis
WR: 147–185 (138–210) nm; $\Phi(\Delta n) = \Phi(N_2) + \Phi(O_2) + \Phi(NO) - \Phi(N_2O) = 1.00 \pm 0.05$; $\Phi(N_2) = 1.44 \pm 0.1$ at moderate pressure near room temperature; $\Phi(N_2) = 1.18$ at 123.6 nm [3]; $\Phi(\Delta n) \sim 0.8$ at 105–120 nm [3]
AM: N_2 analysis, pressure measurement
PP: low absorbance at 150–170 nm ($\varepsilon \leq 30$ 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. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 782, John Wiley, New York (1966).
2. M. Zelikoff and L. M. Aschenbrand. *J. Chem. Phys.* **22**, 1685–1687 (1954).
3. W. E. Groth and H. Schierholz. *Planet. Space Sci.* **1**, 333–336 (1959).
4. N. R. Greiner. *J. Chem. Phys.* **47**, 4373–4377 (1967).
5. A. M. Pravilov and I. O. Shul’pyakov. *High Energy Chem.* **19**, 351–354 (1985).
6. M. C. Dodge and J. Heicklen. *Int. J. Chem. Kinet.* **3**, 269–282 (1971).

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. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 782, John Wiley, New York (1966).
2. J. N. Driscoll and P. Warneck. *Photochem. Photobiol.* **13**, 283–287 (1971).

3. G. R. Powell and D. S. Sethi. *Int. J. Chem. Kinet.* **10**, 1161–1166 (1978).
4. A. K. Davies, K. A. Khan, J. F. McKellar, G. O. Phillips. *Mol. Photochem.* **7**, 389–398 (1976).

G05: Hexafluoroacetone photolysis
WR: 147 nm; Φ(CO) = 0.97 ± 0.05
AM: CO

1. J. J. Magenheimer and R. B. Timmons. *J. Chem. Phys.* **52**, 2790–2791 (1970).
2. G. R. Powell and D. S. Sethi. *Int. J. Chem. Kinet.* **10**, 1161–1166 (1978).

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. L. C. Glasgow and P. Potzinger. *J. Phys. Chem.* **76**, 138–140 (1972).
2. P. Potzinger, L. C. Glasgow, G. von Bünau. *Z. Naturforsch.* **27a**, 628–638 (1972).
3. H. Okabe. *Photochemistry of Small Molecules*, p. 126, Wiley-Interscience, New York (1978).

G07: Trimethylamine photoionization
WR: 147 nm; Φ(ion) = 0.38
AM: ion saturation current, very precise

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

G08: Carbon dioxide photolysis
WR: below 170 nm; Φ(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. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 782, John Wiley, New York (1966).
2. P. Warneck. *J. Opt. Soc. Am.* **56**, 408–409 (1966).
3. H. Okabe. *Photochemistry of Small Molecules*, p. 127, Wiley-Interscience, New York (1978).

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. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 782, John Wiley, New York (1966).
2. R. M. Martin and J. E. Willard. *J. Chem. Phys.* **40**, 2999–3007 (1964).
3. R. P. Roland, M. Bolle, R. W. Anderson. *J. Phys. D: Appl. Phys.* **31**, 1336–1342 (1998).

G10: Phosgene photolysis
WR: 200–280 nm; Φ(CO) = 1.0 ± 0.1 at 254 nm, 1 at 185 nm
AM: CO measurement at liquid nitrogen temperature

1. H. Okabe. *Photochemistry of Small Molecules*, p. 127, Wiley-Interscience, New York (1978).
2. S. Glicker and H. Okabe. *J. Phys. Chem.* **91**, 437–440 (1987).

G11: Nitrosyl chloride photolysis
WR: 230–630 nm; $\Phi(NO) \sim 2.0$
AM: NO analysis

1. cf. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 782, John Wiley, New York (1966).
2. F. I. Vilesov, L. G. Karpov, A. S. Kozlov, A. M. Pravilov, L. G. Smirnova. *High Energy Chem.* **12**, 468–469 (1978).
3. A. M. Pravilov and S. E. Ryabov. *High Energy Chem.* **16**, 331–333 (1982).

G12: Perfluoroglutaryl dichloride [4-chloro-2,2,3,3,4,4-hexafluorobutanoyl 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

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

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

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

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

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

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; $\Phi(cis \rightarrow trans) = \Phi(trans \rightarrow cis) = 0.50 \pm 0.02$ at $p \geq 4$ kPa
AM: GC

1. R. B. Cundall and T. F. Palmer. *Trans. Faraday Soc.* **56**, 1211–1224 (1960).
2. R. B. Cundall. *Prog. React. Kinet.* **2**, 165–215 (1964).
3. M. Termonia and G. R. De Maré. *Chem. Phys. Lett.* **25**, 402–404 (1974).

G17: Propane, Hg-sensitized photolysis
WR: 254 nm; $\Phi(H_2) = 0.581$ at $p = 40$ kPa
AM: pressure measurement

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

G18: Perfluoroacetic anhydride
WR: 254, 265 nm; $\Phi(CO) = 0.29 \pm 0.02$ at 25 °C, 0.34 at 20 °C
AM: CO measurement, Fourier transform infrared (FTIR) spectroscopy

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

G19: Perfluoropropionic anhydride
WR: 254, 265 nm; $\Phi(CO) = 0.24$ at 26 °C, 0.29 at 200 °C
AM: CO measurement

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

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

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

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. E. Cremer and H. Margreiter. *Z. Phys. Chem. (Leipzig)* **199**, 90–99 (1952).
2. E. Cremer and H. Margreiter. *Angew. Chem.* **64**, 427 (1952).

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

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

2.1.3 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; $\Phi = 0.42 \pm 0.04$
AM: GC analysis of methanol degradation and products, ethylene glycol, formaldehyde (2,4-DNPH [2,4-(dinitrophenyl)hydrazine], HPLC), formic acid; DOC = dissolved organic carbon; calibration by cyclooctene actinometer, *cf.* **L02**

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

L02*: *cis*-Cyclooctene *cis–trans* photoisomerization
WR: 185 nm: $\Phi(cis \rightarrow trans) = 0.34 \pm 0.02$ 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. R. Srinivasan and J. A. Ors. *J. Am. Chem. Soc.* **100**, 7089–7091 (1978).
2. H.-P. Schuchmann, C. von Sonntag, R. Srinivasan. *J. Photochem.* **15**, 159–162 (1981).
3. F. Weeke, E. Bastian, G. Schomburg. *Chromatographia* **7**, 163–170 (1974).
4. W. Adam and T. Oppenländer. *Photochem. Photobiol.* **39**, 719–723 (1984).
5. G. Heit, A. Neuner, P.-Y. Saugy, A. M. Braun. *J. Phys. Chem. A* **102**, 5551–5561 (1998).

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

L04: Hydrogen azide (hydrazoic acid) photolysis
WR: 200–260 nm; $\Phi = 1.00 \pm 0.05$ 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.

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

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

1. R. K. Datta and K. N. Rao. *Ind. J. Chem.* **14A**, 122–123 (1976).

L06*: Uranyl oxalate [dioxouranium(VI) 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 photolyzed solution with cerium(IV) sulfate in H_2SO_4 (vs. a nonirradiated blank), or GC (pH dependency [7,10]) for CO, CO_2
PP: Use of commercial Ce(IV) sulfate for titration of nonphotolyzed $C_2O_4^{2-}$ is not recommended because ammonium nitrate impurities may limit the stability of the standardized 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. W. G. Leighton and G. S. Forbes. *J. Am. Chem. Soc.* **52**, 3139–3152 (1930).
2. F. P. Bracket and G. S. Forbes. *J. Am. Chem. Soc.* **55**, 4459–4466 (1933).
3. C. A. Parker. *Proc. R. Soc. (London)* **A220**, 104–116 (1953).
4. C. G. Hatchard and C. A. Parker. *Proc. R. Soc. (London)*, **A235**, 518–536 (1956).
5. J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor, W. Brim. *J. Am. Chem. Soc.* **77**, 5499–5501 (1955).
6. C. A. Discher, P. F. Smith, I. Lippman, R. Turse. *J. Phys. Chem.* **67**, 2501–2503 (1963).
7. D. H. Volman and J. R. Seed. *J. Am. Chem. Soc.* **86**, 5095–5098 (1964).
8. J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 787, John Wiley, New York (1966).
9. S. L. Murov. *Handbook of Photochemistry*, 2nd ed., Sect. 13, p. 305, Marcel Dekker, New York (1993).
10. L. J. Heidt, G. W. Tregay, F. A. Middleton, Jr. *J. Phys. Chem.* **74**, 1876–1882 (1970); K. Porter and D. H. Volman. *J. Am. Chem. Soc.* **84**, 2011–2012 (1962).
11. H. A. Taylor. In *Analytical Photochemistry and Photochemical Analysis*, J. M. Fitzgerald (Ed.), p. 91, Marcel Dekker, New York (1971).
12. D. F. Eaton. Ph.D. thesis, p. 120, California Institute of Technology (1972).
13. P. de Mayo and H. Shizuka. *Creation and Detection of the Excited State*, W. R. Ware (Ed.) **4**, 140, Marcel Dekker, New York (1976).
14. G. F. Smith and W. H. Fly. *Anal. Chem.* **21**, 1233–1237 (1949).
15. F. J. Benítez, J. Beltrán–Heredia, T. González, J. L. Acero. *Water Res.* **28**, 2095–2100 (1994).

16. G. H. Rossetti, E. D. Albizzati, O. M. Alfano. *Ind. Eng. Chem. Res.* **37**, 3592–3601 (1998).
17. A. Sánchez Mirón, E. Molina Grima, J. M. Fernández Sevilla, Y. Chisti, F. García Camacho. *J. Appl. Phycol.* **12**, 385–394 (2000).

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

L07: Malachite green leucocyanide (4-dimethylamino)-α-[4-(dimethylamino)phenyl]-α-phenylbenzeneacetonitrile [2,2-bis(4-dimethylamino)phenyl]-2-phenylacetonitrile] 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. J. G. Calvert and H. J. L. Rechen. *J. Am. Chem. Soc.* **74**, 2101–2103 (1952).
2. G. J. Fisher, J. C. LeBlanc, H. E. Johns. *Photochem. Photobiol.* **6**, 757–767 (1967).
3. H. A. Taylor. In *Analytical Photochemistry and Photochemical Analysis*, J. M. Fitzgerald (Ed.), pp. 91–115, Marcel Dekker, New York (1971).

PP: Care should be taken to avoid product accumulation.

1. On paper: L. Chalkley. *J. Opt. Soc. Am.* **42**, 387–392 (1952).
2. In thin films: H. Nakazumi, K. Makita, R. Nagashiro. *J. Sol.-Gel. Sci. Technol.* **8**, 901–909 (1997).

L08: Chloroacetic acid photohydrolysis

WR: ≤270 nm; $\Phi(\lambda) = 0.31$ 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. R. N. Smith, P. A. Leighton, W. G. Leighton. *J. Am. Chem. Soc.* **61**, 2299–2301 (1939).
2. L. B. Thomas. *J. Am. Chem. Soc.* **62**, 1879–1880 (1940).
3. W. Kemula and A. Grabowska. *Roczn. Chemii* **29**, 834–838 (1955).
4. H. A. Taylor. In *Analytical Photochemistry and Photochemical Analysis*, J. M. Fitzgerald (Ed.), pp. 91–115, Marcel Dekker, New York (1971).
5. M. Neumann-Spallart and N. Getoff. *Radiat. Phys. Chem.* **13**, 101–105 (1979).

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

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

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

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

$\Phi(\lambda)$ 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. P. A. Swenson and R. B. Setlow. *Photochem. Photobiol.* **2**, 419–434 (1963).
2. G. J. Fisher and H. Johns. In *Photochemistry and Photobiology of Nucleic Acids*, Vol. 1, S. Y. Wang (Ed.), Chap. 4, pp. 169–224, Academic Press, New York (1976).
3. E. V. Khoroshilova, D. N. Nikogosyan. *J. Photochem. Photobiol., B* **5**, 413–427 (1990).
4. H. Görner. *J. Photochem. Photobiol., B* **10**, 91–110 (1991).
5. G. G. Gurzadyan and H. Görner. *Photochem. Photobiol.* **60**, 323–332 (1994).
6. C. von Sonntag and H.-P. Schuchmann. *J. Water SRT–Aqua* **41**, 67–74 (1992).
7. R. S. Nohr, J. G. MacDonald, U. Kogelschatz, G. Mark, H.-P. Schuchmann, C. von Sonntag. *J. Photochem. Photobiol., A* **79**, 141–149 (1994).
8. G. G. Gurzadyan and H. Görner. *Photochem. Photobiol.* **63**, 143–153 (1996).

9. J.-Y. Zhang, I. W. Boyd, H. Esrom. *Appl. Surf. Sci.* **109/110**, 482–486 (1997); *Chem. Abstr.* 126–256881/19.
10. K. G. Linden and J. L. Darby. *J. Environ. Eng*. **123**, 1142–1149 (1997).

L10: 1,3-Dimethyluracil photohydration in aqueous solution
WR: 240–280 nm; $\Phi(\lambda) = 0.0130 \pm 0.0007$ in water (254 nm); 0.0140 (240 nm), 0.0111 (248 nm), 0.0138 (265 nm), 0.0147 (280 nm) at 0.9×10^{-3} M in 10^{-2} M phosphate buffer, $\Phi(\text{average}) = 0.0134 \pm 0.0016$; at 6×10^{-5} M, $\Phi(\text{average}) = 0.0139 \pm 0.0005$
AM: absorbance at 266 nm

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

L11*: Azobenzene {Actinochrome 2R (245/440)} [diazenediyldibenzene] photoisomerization (reusable)
WR: 230–460 nm; $\Phi(cis \rightarrow trans) = 0.4$–$0.5$; $\Phi(trans \rightarrow cis) = 0.1$–$0.2$ in methanol or isooctane [2,2,4-trimethylpentane] different for the two bands; S_{ac} about 10^3 dm^3 mol^{-1} cm^{-1}
AM: absorbance at 358 nm; HPLC
PP: 6.4×10^{-4} M in CH_3OH; $\Phi(trans \rightarrow cis) = 0.14$ in CH_3OH, 0.24 in isooctane; $\Phi(cis \rightarrow trans) = 0.48$ in CH_3OH, 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. G. Zimmerman, L.-Y. Chow, U.-J. Paik. *J. Am. Chem. Soc.* **80**, 3528–3531 (1958).
2. G. Gauglitz. *J. Photochem.* **5**, 41–47 (1976).
3. G. Gauglitz and S. Hubig. *J. Photochem.* **15**, 255–257 (1981).
4. G. Gauglitz and S. Hubig. *J. Photochem.* **30**, 121–125 (1985).
5. J. Drabek, I. Cepciansky, J. Poskocil. *Chem. Listy* **78**, 94–98 (1984).
6. G. Gauglitz and S. Hubig. *Z. Phys. Chem. N. F.* **139**, 237–246 (1984).
7. G. Persy and J. Wirz. *EPA Newslett.* **29**, 45–46 (1987).

PP: Quantum yields for the *cis* → *trans* reaction at 313 nm in various solvents were redetermined: $\Phi = (0.35 \pm 0.030)$ 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:

8. N. Siampiringue, G. Guyot, S. Monti, P. Bortolus. *J. Photochem.* **37**, 185–188 (1987).
9. Application to polychromatic radiation (medium pressure Hg-arc plus filter solutions): A. Gahr, L. Weil, R. Nießner. *Water Res.* **29**, 2125–2137 (1995).

L12: 1-Deazapurine *N*(3)-oxide [imidazo[4,5-*b*]pyridine 4-oxide] or 1-methyl-1-deazapurine *N*(3)-oxide [6-methylimidazo[4,5-*b*]pyridine 4-oxide] fluorogenic photorearrangement
WR: 250–310 nm; 1 mM solutions in 10 mM phosphate buffer, pH 7; $\Phi = 0.13$–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

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

L13*: Potassium peroxodisulfate/*tert*-butyl alcohol [2-methylpropan-2-ol] 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 < ± 5 %; independent of photon irradiance $E_{n,\mathrm{p}}$ between $5 \times 10^{-6} - 2 \times 10^{-5}$ einstein $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$

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

PP: freshly prepared oxygenated actinometer solution: 10×10^{-3} M $K_2S_2O_8$ 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 apparently higher Φ values due to thermal decomposition of the peroxo salt.

1. G. Mark, M. N. Schuchmann, H.-P. Schuchmann, C. von Sonntag. *J. Photochem. Photobiol., A* **55**, 157–168 (1990).
2. G. Mark, M. N. Schuchmann, H.-P. Schuchmann, C. von Sonntag. *J. Water SRT–Aqua* **39**, 309–313 (1990).
3. O. Hoyer, R. Kryschi, I. Piecha, G. Mark, M. N. Schuchmann, H.-P. Schuchmann, C. von Sonntag. *J. Water SRT–Aqua* **41**, 75–81 (1992).

L14: Potassium iodide in dinitrogen oxide (N_2O)-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 0.1 M borate buffer pH 4, N_2O bubbling (electron scavenger); gradual decrease (1–2 % per hour) of triiodide.

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

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; $\Phi(\lambda)$ increases at $\lambda < 254$ nm and decreases at $\lambda > 254$ nm [3].

1. R. O. Rahn. *Photochem. Photobiol.* **66**, 450–455 (1997); **erratum**: *ibid* **66**, 885 (1997).
2. R. O. Rahn, P. Xu, S. L. Miller. *Photochem. Photobiol.* **70**, 314–318 (1999).
3. R. O. Rahn, M. I. Stephan, J. R. Bolton, E. Goren, P.-S. Shaw, K. R. Lykke. *Photochem. Photobiol.* **78**, 146–152 (2003).

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. W. J. Leigh, C. J. Bradaric, C. Kerst, J. H. Banisch. *Organometallics* **15**, 2246–2253 (1996).
2. W. J. Leigh, R. Boukherroub, C. J. Bradaric, C. C. Cserti, J. M. Schmeisser. *Can. J. Chem.* **77**, 1136–1147 (1999).

L17: Cyclohepta-1,3-diene photoisomerization
WR: 254 nm; *Φ* = 0.48 ± 0.01 in ethanol
AM: absorbance at 246 nm

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

L18: Iodomethane photoexchange with $^{132}I_2$
WR: 254 nm; *Φ* = 1.0
AM: radiochemical

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

L19: 1,2,3,4-Tetraphenylcyclobutane (TPCB) photocycloreversion
WR: 250–270 nm, continuous irradiation or 266 nm **laser** flashes ($<10^{17}$ photons per pulse); *Φ* = 0.29 ± 0.01 in 1-chlorobutane or methylcyclohexane (MCH)
AM: absorbance at 295 nm (*trans*-stilbene)
PP: no effect of temperature (270–310 K, MCH) or dissolved oxygen (MCH)

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

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); *Φ* = 0.12 ± 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)

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

L21* Heterocoerdianthrone endoperoxide {Actinochrome 1R (248/334)} [4b,12b-Epidioxy-dibenzo[*a,j*]perylene-8,16-dione] photoreversible photodissociation
WR: 248–334 nm for the dissociation; *Φ* = 0.27 ± 0.01 in dichloromethane (2×10^{-3} M) independent of λ between 253 and 302 nm; S_{ac} = (7770 ± 200) $dm^3\ mol^{-1}\ cm^{-1}$ (253–302 nm), $S_{ac}(\lambda)$ = 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. The compound is no longer commercially available.

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

L22: Azoxybenzene [diphenyldiazene oxide] → 2-hydroxyazobenzene [2-(phenyldiazenyl)phenol] photorearrangement
In solid phase, cf. **S05**
WR: 250–350 nm: *Φ* ~ 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. N. J. Bunce, J. LaMarre, S. P. Vaish. *Photochem. Photobiol.* **39**, 531–533 (1984).
2. cf. H. Mauser, G. Gauglitz, F. Stier. *Liebigs Ann. Chem.* **739**, 84–94 (1970).

L23: 3-(2-Hydroxyphenyl)-2-propenoic acid [prop-2-enoic acid] (*o*-coumaric acid dianion) photoisomerization in aqueous solution
cis → *trans* reaction
WR: 254–300 nm: $\Phi(cis \rightarrow trans) = 0.52 \pm 0.05$; 313–400 nm: $\Phi(cis \rightarrow trans) = 0.75 \pm 0.05$
trans → *cis* reaction
WR: 254–300 and 350–400 nm: $\Phi(trans \rightarrow cis) = 0.10 \pm 0.01$
AM: absorbance, fluorescence at 492 nm
PP: Not recommended as a reliable actinometer; strong dependence on pH, O_2, and counterion (Cl^-) concentration

1. G. Perbet, L.-M. Coulangeon, P. Boule, J. Lemaire. *J. Chim. Phys.* **75**, 1096–1104 (1978).
2. G. Guyot, C. Pizzocaro, J. Lemaire. *J. Photochem.* **36**, 11–26 (1987).

L24: Adenine photolysis
WR: 254–300 nm; Φ = 0.0027–0.0029 (deoxygenated), 0.0081–0.0085 (aerated); Φ (chromophore loss) ≈ 0.1×10^{-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. M. Rivera. *J. Chem. Educ.* **66**, 1049–1051 (1989).
2. 193 nm laser and 254 nm continuous irradiation: G. G. Gurzadyan and H. Görner. *Photochem. Photobiol.* **60**, 323–332 (1994).

L25: 2-Hydroxy-4′-(dimethylamino)chalcone [1-[4-(dimethylamino)phenyl]-3-(2-hydroxyphenyl)-prop-2-en-1-one] to 4′-(dimethylamino)flavylium ion photoconversion
WR: 254–366 nm; $\Phi(\lambda) = 0.23 \pm 0.01$ (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: $(0.075–10) \times 10^{-3}$ M chalcone, 5×10^{-3} M *p*-toluenesulfonic acid [4-methylbenzenesulfonic 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. R. Matsushima, N. Suzuki, T. Muarakami, M. Morioka. *J. Photochem. Photobiol., A* **109**, 91–94 (1997).
2. cf. R: Matsushima, H. Mizuno, A. Kajiura. *Bull. Chem. Soc. Jpn.* **67**, 1762–1764 (1994).

L26: Stilbenes *cis* → *trans* photoisomerization
WR: 254–366 nm; quantum yields depend on stilbene substitution and solvent
AM: absorbance, GC

1. J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener, E. D. Megarity. *J. Am. Chem. Soc.* **101**, 2982–2996 (1979).
2. J. Saltiel and J.-L. Charlton. In *Rearrangements in Ground and Excited States*, P. de Mayo (Ed.) **3**, pp. 25–90, Academic Press, New York (1980).
3. H. Görner. *Ber. Bunsen-Ges. Phys. Chem.* **88**, 1199–1208 (1984).
4. T.-I. Ho, T.-M. Su, T.-C. Hwang. *J. Photochem. Photobiol., A* **41**, 293–298 (1988).
5. For quantum yields, cf. H. Görner and H. J. Kuhn. *Adv. Photochem.* D. C. Neckers, D. H. Volman, C. von Bünau (Eds.), **19**, 1–117 (1995).

L27: 1,2-Dimethoxy-4-nitrobenzene → 2-methoxy-5-nitrophenolate, photohydrolysis
WR: 254–365 nm (applied to 308 nm XeCl-excimer lamp, [2]); *Φ* = 0.116 ± 0.002 (0.136 mM in 0.5 M aqueous KOH)
AM: absorbance of product 2-methoxy-5-nitrophenolate

1. L. Pavlickova, P. Kuzmic, M. Soucek. *Collect. Czech. Chem. Commun.* **51**, 368–374 (1986).
2. J.-Y. Zhang, H. Esrom, I. W. Boyd. *Appl. Surf. Sci.* **138–139**, 315–319 (1999); *Chem. Abstr.* **130**, 259437.

L28: *p*-Benzoquinone photoreduction in aqueous solution
WR: 260–380 nm, *Φ* = 0.47 ± 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. A. I. Ononye and J. R. Bolton. *J. Phys. Chem.* **90**, 6270–6274 (1986).
2. T. L. Ho, J. R. Bolton, E. Lipczynska-Kochany. *J. Adv. Oxid. Technol.* **1**, 170–178 (1996).

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

L29: Phenylglyoxylic acid photodecarboxylation
WR: 254–405 nm; *Φ* = 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 $\lambda_{\text{obs}} \leq 370$ 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. A. Defoin, R. Defoin-Straatmann, K. Hildenbrand, E. Bittersmann, D. Kreft, H. J. Kuhn. *J. Photochem.* **33**, 237–255 (1986).
2. A. Defoin and H. J. Kuhn. *EPA Newslett.* **26**, 23–25 (1986).
3. H. J. Kuhn and H. Görner. *J. Phys. Chem.* **92**, 6208–6219 (1988).
4. Photorheological effects in micellar solution: T. Wolff, F. Schmidt, G. von Bünau. *J. Photochem. Photobiol., A* **48**, 435–446 (1989).

L30: Hydrogen peroxide photolysis sensitized by uranyl sulfate [dioxouranium(VI) sulfate]
WR: 250–450 nm; *Φ* = 1.30 ± 0.03 (20 °C) in 3 M H_2SO_4; temperature coefficient +0.0095/°C
AM: O_2 volumetric, H_2O_2 consumption

1. G. O. Schenck and W. Haubold. Referred to in: G. O. Schenck. *Angew. Chem.* **69**, 579–599 (1957).
2. G. Folcher, J. Paris, E. Saito. *Nouv. J. Chim.* **7**, 703–709 (1983).
3. cf. I. Nicole, J. DeLaat, M. Dore, J. P. Duguet, C. Bonnel. *Water Res.* **24**, 157–168 (1990).
4. For primary *Φ* of H_2O_2 decomposition: cf. J. L. Weeks and M. S. Matheson. *J. Am. Chem. Soc.* **78**, 1273–1278 (1956); F. S. Dainton. *J. Am. Chem. Soc.* **78**, 1278–1279 (1956); T. L. Ho, J. R. Bolton, E. Lipczynska-Kochany. *J. Adv. Oxid. Technol.* **1**, 170–178 (1996).

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

L31*: Potassium ferrioxalate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ [potassium tris(oxalato)ferrate(III) trihydrate] 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 [tris(1,10-phenanthroline)iron(II)] 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 premixed 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. C. G. Hatchard and C. A. Parker. *Proc. R. Soc. London* **A235**, 518–536 (1956); part I: C. A. Parker. *Proc. R. Soc. London* **A220**, 104–116 (1953).
2. J. H. Baxendale and N. K. Bridge. *J. Phys. Chem.* **59**, 783–788 (1955).
3. C. E. Bricker and S. S. Schonberg. *Anal. Chem.* **30**, 922–928 (1958).
4. J. Lee and H. H. Seliger. *J. Chem. Phys.* **40**, 519–523 (1964).
5. J. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 783, John Wiley, New York (1966).
6. E. E. Wegner and A. W. Adamson. *J. Am. Chem. Soc.* **88**, 394–404 (1966).
7. H. P. Wolf, J. J. Bohning, P. A. Schnieper, K. Weiss. *Photochem. Photobiol.* **6**, 321–329 (1967).
8. C. A. Parker. *Photoluminescence of Solutions*, pp. 208–214, Elsevier, Amsterdam (1968).
9. H. A. Taylor. “Analytical methods and techniques for actinometry”, in *Analytical Photochemistry and Photochemical Analysis,* J. M. Fitzgerald (Ed.), pp. 91–115, Marcel Dekker, New York (1971).
10. K. C. Kurien. *J. Chem. Soc.* B, 2081–2082 (1971).
11. M. S. Wrighton and S. Witz. *Mol. Photochem.* **3**, 387–394 (1972).
12. S. L. Murov. *Handbook of Photochemistry*, 2nd ed., Sect. 13, pp. 299–313, Marcel Dekker, New York (1993).
13. P. de Mayo and H. Shizuka. “Measurement of reaction quantum yields”, *Creation and Detection of the Excited State*, W. R. Ware (Ed.) **4**, 139–216 (1976).
14. W. D. Bowman and J. N. Demas. *J. Phys. Chem.* **80**, 2434–2435 (1976).
15. D. E. Nicodem, M. L. P. F. Cabral, J. C. N. Ferreira. *Mol. Photochem.* **8**, 213–238 (1977).
16. P. Thomas, M. Benedix, H. Hennig. *Z. Chem.* **17**, 114–115 (1977).
17. E. Fernández, J. M. Figuera, A. Tobar. *J. Photochem.* **11**, 69–71 (1979).
18. A. D. Baker, A. Casadavell, H. D. Gafney, M. Gellender. *J. Chem. Educ.* **57**, 314–315 (1980).
19. H. Gruter. *J. Appl. Phys.* **51**, 5204–5206 (1980).
20. J. S. Connolly and T. H. Meyer. *Photochem. Photobiol.* **34**, 145–146 (1981).
21. E. W. Vitz and E. Boschmann. *J. Chem. Educ.* **58**, 655 (1981).
22. J. N. Demas, W. D. Bowman, E. F. Zalewski, R. A. Velapoldi. *J. Phys. Chem.* **85**, 2766–2771 (1981).
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24. E. A. Wolfenden, A. D. Q. Agnew, D. R. Causton. *Acta Oecolog. Oecol. Plant.* **3**, 101–111 (1982).
25. D. E. Nicodem and O. M. V. Aquilera. *J. Photochem.* **21**, 189–193 (1983).
26. A. D. Kirk and C. Namasivayam. *Anal. Chem.* **55**, 2428–2429 (1983).
27. G. Gauglitz. *EPA Newslett.* **19**, 49–53 (1983).
28. E. Fischer. *EPA Newslett.* **21**, 33–34 (1984).
29. A. M. Braun, M.-T. Maurette, E. Oliveros. *Technologie Photochimique*, pp. 43–96, Presses Polytechniques Romandes, Lausanne (1986), *idem, Photochemical Technology*, pp. 77–81, John Wiley, Chichester (1991).

30. L. Vincze and S. Papp. *J. Photochem.* **36**, 289–296 (1987).
31. G. D. Harris, V. D. Adams, W. M. Moore, D. L. Sorensen. *J. Environ. Eng.* **113**, 612–627 (1987).
32. H.-J. Timpe, S. Ulrich, S. Ali. *J. Photochem. Photobiol. A: Chem.* **61**, 77–89 (1991) (actinometry in an EPR tube).
33. Y. Izumi. *Reza Kenkyu* **19**, 247–253 (1991); *Chem. Abstr.* **115** 193378/18.
34. L. Sun and J. R. Bolton. *J. Phys. Chem.* **100**, 4127–4134 (1996) (EPR flat cell).
35. L. Vincze, T. J. Kemp, P. R. Unwin. *J. Photochem. Photobiol., A* **123**, 7–13 (1999) (flow actinometer).
36. R. O. Rahn, M. I. Stefan, J. R. Bolton, E. Goren, P.-S. Shaw, K. R. Lykke. *Photochem. Photobiol.* **78**, 146–152 (2003).
37. S. M. Fonseca, S. Ahmed, T. J. Kemp, P. R. Unwin. *Photochem. Photobiol Sci.* **2** (2), 98–103 (2003) (microelectrochemical actinometer).

L32*: *Laser* 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): R. Bensasson, C. R. Goldschmidt, E. J. Land, T. G. Truscott. *Photochem. Photobiol.* **28**, 277–281 (1978).
2. 308 nm: (benzophenone-4-carboxylate in aqueous solution): J. von Sonntag. *J. Photochem. Photobiol., A* **126**, 1–5 (1999).
3. 308 nm, 355 nm (benzophenone, benzoins): C. García, G. A. Smith, W. G. McGimpsey, I. E. Kochevar, R. W. Redmond. *J. Am. Chem. Soc.* **117**, 10871–10878 (1995); N. K. Shestra, E. J. Yagi, Y. Takatori, A. Kawai, Y. Kajii, K. Shibuya, K. Obi. *J. Photochem. Photobiol., A* **116**, 179–185 (1998).
4. 337 nm (benzophenone-4-carboxylate in aqueous solution): B. Marciniak, E. Andrzejewska, G. L. Hug. *J. Photochem. Photobiol., A* **112**, 21–28 (1998).
5. 347 nm (benzophenone, ZnTPP in toluene and other solvents): L. V. Romashov, Yu. I. Kiryukhin, K. S. Bagdasar'yan. *High Energy Chem.* **12**, 132–134 (1978); I. Carmichael and G. L. Hug. *J. Phys. Chem. Ref. Data* **15**, 1–250 (1986); J. K. Hurley, N. Sinai, H. Linschitz. *Photochem. Photobiol.* **38**, 9–14 (1983).
6. 347 nm (benzophenone-4-carboxylate in aqueous solution): J. K. Hurley, H. Linschitz, A. Treinin. *J. Phys. Chem.* **92**, 5151–5159 (1988).
7. 353 nm (all-*trans*-retinal in hexane): R. Bensasson, C. R. Goldschmidt, E. J. Land, T. G. Truscott. *Photochem. Photobiol.* **28**, 277–281 (1978).
8. 355 nm, 532 nm [$Ru(bpy)_3{}^{2+}$ in aqueous solutions and polar organic solvents]: A. Yoshimura, M. Z. Hoffman, H. Sun. *J. Photochem. Photobiol., A* **70**, 29–33 (1993).
9. cf. R. Bonneau, I. Carmichael, G. L. Hug. *Pure Appl. Chem.* **63**, 289–299 (1991).
10. cf. R. Bonneau, J. Wirz, A. D. Zuberbühler. *Pure Appl. Chem.* **69**, 979–992 (1997). See: <http://www.rcdc.nd.edu/browse_compil.html#browse_access>.

L33: 2,3-Dimethylbut-2-ene, sensitized photooxygenation
Especially designed for high-power pulse and cw **lasers**
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. J. N. Demas, E. W. Harris, R. P. McBride. In *Lasers in Physics, Chemistry, and Biophysics, Proc. Int. Meet. Soc. Chim. Phys.* **27**, J. Joussot-Dubien (Ed.), pp. 477–484, Elsevier, Amsterdam (1975).
2. J. N. Demas, R. P. McBride, E. W. Harris. *J. Phys. Chem.* **80**, 2248–2253 (1976).

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

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

L35: *o*-Nitrobenzaldehyde → *o*-nitrosobenzoic acid photoisomerization
WR: 300–410 nm; $\Phi = 0.5$ in acetone and CH_2Cl_2, independent of temperature. Same Φ in all phases (cf. **S06**)
AM: GC; LC; IR NO_2 band disappearance

1. P. Leighton and F. A. Lucy. *J. Chem. Phys.* **2**, 756–759 (1934).
2. J. N. Pitts, Jr., J. M. Vernon, J. K. S. Wan. *Int. J. Air Water Pollut.* **9**, 595–600 (1965).
3. K. L. Willett and R. A. Hites. *J. Chem. Ed.* **77**, 900–902 (2000).
4. J. M. Allen, S. A. Allen, J. Dreiman, S. W. Baertschi. *Photochem. Photobiol.* **69**, 17S–18S (1999); 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. R. G. E. Morales, G. P. Jara, S. Cabrera. *Limnol. Oceanogr.* **38**, 703–705 (1993); for the determination of solar UV radiation and penetration in waters.
6. J. von Sonntag and W. Knolle. *J. Photochem. Photobiol., A* **136**, 133–139 (2000); for the determination of quantum yields by conductimetry; $\Phi(\lambda) = 0.5$ at 308 nm, confirmed against ferrioxalate actinometer (**L31***).

L36: Sodium nitrate/benzoic acid in aqueous solution
WR: 305–320 nm; $\Phi = 0.00152 \pm 0.00004$ (scavenging product salicylic acid), $\Phi = 0.00105 \pm 0.00003$ (formation of *p*-hydroxybenzoic acid)
AM: HPLC analysis (with absorbance and fluorescence detection) of salicylic acid and *m*/*p*-hydroxybenzoic acid or batch fluorescence ($\lambda_{exc} = 305$ nm, $\lambda_{em} = 410$ 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: J. J. Jankowski, D. J. Kleber, K. Mopper. *Photochem. Photobiol.* **70**, 319–328 (1999).
2. cf. also: G. Mark, H.-G. Korth, H.-P. Schuchmann, C. von Sonntag. *J. Photochem. Photobiol., A* **101**, 89–103 (1996).
3. 172 nm: cf.*:* M. C. González and A. M. Braun. *Res. Chem. Intermed.* **21**, 837–859 (1995).

L37: Benzophenone/benzhydrol [diphenylmethanol] photoreduction in benzene
WR: 300–390 nm; relative method, no predetermined Φ
AM: differential absorbance

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

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. D. R. Coulson and N. C. Yang. *J. Am. Chem. Soc.* **88**, 4511–4513 (1966).
2. P. J. Wagner. *Tetrahedron Lett.* 5385–5388 (1968).
3. S. L. Murov. *Handbook of Photochemistry*, 2nd ed., Sect. 13, p. 309, Marcel Dekker, New York (1993).

L39: Butyrophenone [1-phenylbutan-1-one] photoelimination

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

AM: GC, products acetophenone and ethene

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

L40: Valerophenone [1-phenylpentan-1-one] photolysis

WR: 313 nm, *Φ* = 0.30–0.35 in benzene; 290–330 nm: in aqueous solution *Φ* ~ 0.98 ± 0.04 (cleavage plus cyclization), *Φ* = 0.65 ± 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. P. J. Wagner and A. E. Kemppainen. *J. Am. Chem. Soc.* **94**, 7495–7499 (1972); cf. 7489–7494.
2. W. Amrein, J. Gloor, K. Schaffner. *Chimia* **28**, 185–188 (1974).
3. V. Wintgens, L. J. Johnston, J. C. Scaiano. *J. Am. Chem. Soc.* **110**, 511–517 (1988).
4. R. G. Zepp, M. M. Gumz, W. L. Miller, H. Gao. *J. Phys. Chem. A* **102**, 5716–5723 (1998).

L41: 2-Methyl-2-phenylpropanal photolysis.

WR: 313 nm; *Φ* = 0.83 in isooctane

AM: GC; products isopropylbenzene, CO, besides cyclobutanols

1. W. Amrein, J. Gloor, K. Schaffner. *Chimia* **28**, 185–188 (1974).
2. H. Küntzel, K. Wolf, K. Schaffner. *Helv. Chim. Acta* **54**, 868–897 (1971).

L42: *trans*-2-Nitrocinnamaldehyde [*trans*-3-(2-nitrophenyl)prop-2-en-al] 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. E. Bovina et al., oral commun., *2nd Intern. Meet. Photostability of Drugs*, 14–16 Sept. 1997, Pavia, Italy; A. Albini, *EPA Newslett.* **61**, 85–86 (1997).
2. E. Bovina, P. De Filippis, V. Cavrini, R. Ballardini. *Spec. Publ.–R. Soc. Chem.* **225** (Drugs: Photochemistry and Photostability) 305–316 (1998); *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. S. L. Murov. *Handbook of Photochemistry*, 2nd ed., Sect. 13, p. 310, Marcel Dekker, New York (1993)
2. G. F. Vesley. *Mol. Photochem.* **3**, 193–200 (1971).

L44: Cyclohexa-1,3-diene, sensitized photodimerization
WR: 313, 366 nm: $\Phi = 0.97$ in benzene
AM: GC

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

L45*: Fulgide reversible photocyclization:
Aberchrome 540 [(*E*)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)succinic anhydride] $\rightleftharpoons$ Aberchrome 540P [7,7a-dihydro-2,4,7,7,7a-pentamethylbenzo[*b*]furan-5,6-dicarboxylic anhydride]
WR: 310–375 nm (reversible with white light); $\Phi = 0.20$ in toluene solution (5×10^{-3}–10^{-2} M); $S_{\mathrm{ac}}(\lambda) = 1640\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 494 nm, $1214\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 343 nm; $\Phi = 0.18$ (365 nm, in toluene or ethylacetate [10e]), $\Phi = 0.20$ (365 nm, *n*-hexane [10e])
WR: back reaction 435–535 nm; $\Phi(\lambda) = 0.073$ (436 nm), 0.0594 (494 nm), 0.0470 (546 nm), linearly dependent on λ; $S_{\mathrm{ac}}(\lambda) = 487\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 494 nm; $\Phi = 0.09$ (436 nm, in toluene [10e]), $\Phi = 0.06$ (436 nm, in ethylacetate [10e]), $\Phi = 0.11$ (436 nm, *n*-hexane [10e])
AM: absorbance at 494 nm [$\varepsilon(494\ \mathrm{nm}) = 8200\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$] or at 343 nm [$\varepsilon(343\ \mathrm{nm}) = 6077\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$]
PP: reproducibility ±1 %; precision ±3 %; other solvents possible; degassing desirable while not essential; no conversion limit, but only small *A* changes necessary
PP: Aberchrome 540 is a widely used actinometer. However, 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: Aberchrome 540 is no longer commercially available.

1. H. G. Heller. *Chem. Ind.* 193 (1978); Brit. Patent 7/1464603, U.S. Patent 9/719,254.
2. H. G. Heller and J. R. Langan. *J. Chem. Soc., Perkin Trans. 1* 341–343 (1981).
3. H. G. Heller and J. R. Langan. *EPA Newslett.* Oct. 71–73 (1981).
4. Use in one- and two-**laser** experiments: V. Wintgens, L. J. Johnston, J. C. Scaiano. *J. Am. Chem. Soc.* **110**, 511–517 (1988).
5. J. Whittal. In *Photochromism, Molecules and Systems*, H. Dürr and H. Bouas-Laurent (Eds.), Chap. 9, pp. 467–492, Elsevier, Amsterdam (1990).
6. Quantum yields of $E \rightarrow Z$ and $Z \rightarrow E$ isomerization and *E*–cyclization and back reaction in various solvents and polymers: Y. Yokoyama, H. Hayata, H. Ito, Y. Kurita. *Bull. Chem. Soc. Jpn.* **63**, 1607–1610 (1990); V. Deblauwe and G. Smets. *Makromol. Chem.* **189**, 2503–2512 (1988).
7. Details concerning bleaching reaction: cf. A. P. Glaze, H. G. Heller, J. Whittal. *J. Chem. Soc. Perkin Trans. 2* 591–594 (1992); solvent effects on bleaching: M. Rappon and R. T. Syvitski. *J. Photochem. Photobiol., A* **94**, 243–247 (1996).
8. Kinetics of photodecolouration in polymer films, polystyrene, PMMA, PVA, and others: M. Rappon, A. Chuenarm, A. J. Duggal, H. Gill, O. Bhaovibul, R. T. Syvitski. *Eur. Polym. J.* **27**, 365–370 (1991); M. Rappon, R. T. Syvitski, A. Chuenarm. *Eur. Polym. J.* **28**, 399–403 (1992).
9. Electronic substituent effects on quantum yields: A. Tomoda, A. Kaneko, H. Tsuboi, R. Matsushima. *Bull. Chem. Soc. Jpn.* **66**, 330–333 (1993).

Critical discussion:

10a. P. Boule and J. F. Pilichowski. *EPA Newslett.* **47**, 42–43 (1993).
10b. *Reply*: H. G. Heller. *EPA Newslett.* **47**, 44 (1993).
10c. P. Boule and J. F. Pilichowski. *J. Photochem. Photobiol., A* **71**, 51–53 (1993).
10d. *Photokinetics*: Z. Guo, G. Wang, Y. Tang, X. Song. *J. Photochem. Photobiol., A* **88**, 31–34 (1995).
10e. *New quantum yields*: E. Uhlmann and G. Gauglitz. *J. Photochem. Photobiol., A* **98**, 45–49 (1996).

11. *Laser actinometry,* e.g.: J. C. Scaiano, B. R. Arnold, W. G. McGimpsey. *J. Phys. Chem.* **98**, 5431–5434 (1994); 12. C. García, G. A. Smith, W. G. McGimpsey, I. E. Kochevar, R. W. Redmond. *J. Am. Chem. Soc.* **117**, 10871–10878 (1995).

L46: Potassium reineckate, $K[Cr(NH_3)_2(CNS)_4]$ [potassium diaminetetrakis(thiocyanato-N) chromate] 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; $S_{ac}(\lambda) = 30.5$ dm^3 mol^{-1} cm^{-1} at 520 nm; $\varepsilon(520\text{ nm}) = (110.7 \pm 2.3)$ dm^3 mol^{-1} cm^{-1}; $\varepsilon(542\text{ nm}) = (36.2 \pm 1.7)$ dm^3 mol^{-1} cm^{-1}, $\varepsilon(392\text{ nm}) = (96.3 \pm 2.5)$ dm^3 mol^{-1} cm^{-1} [4]
AM: absorbance at 450 nm of iron(III) thiocyanate complex {$\varepsilon = (3400 \pm 200)$ dm^3 mol^{-1} cm^{-1}[7], **note**: *diff. from* [1]}
PP: $\Phi(\lambda)$ = 0.291 (316 nm), 0.388 (350 nm), 0.335 (366 nm), 0.316 (392 nm), 0.310 (416 nm), 0.311 (452 nm), 0.299 (504 nm), 0.286 (520 nm), 0.282 (545 nm), 0.270 (577 and 585 nm), 0.276 (600 nm), 0.271 (676 nm), 0.284 (713 nm), 0.302 (735 nm), 0.273 (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. E. E. Wegner and A. W. Adamson. *J. Am. Chem. Soc.* **88**, 394–404 (1966); cf. G. H. Searle, G. S. Bull, D. A. House. *J. Chem. Educ.* **66**, 605–608 (1989).
2. P. de Mayo and P. H. Shizuka. In *Creation and Detection of the Excited State*, W. R. Ware (Ed.), **4**, pp. 139–216, Marcel Dekker, New York (1976).
3. J. N. Demas. In *Creation and Detection of the Excited State*, W. R. Ware (Ed.) **4**, pp. 1–62, Marcel Dekker, New York (1976).
4. S. Hubig. *Diplomarbeit* (G. Gauglitz) Tübingen (1980).
5. J. Szychlinski, P. Bilski, K. Martuszewski, J. Blazejowski. *Analyst* **114**, 739–741 (1989).
6. E. Görgens, R. Hänsel, H. Böttcher. *Exp. Techn. Physik* **35**, 201–212 (1987).
7. Improved preparation of Reinecke's salt, application to biophotoreactor: J.-F. Cornet, A. Marty, J.-B. Gros. *Biotechnol. Prog.* **13**, 408–415 (1997).

L47*: 9,10-Dimethylanthracene self-sensitized photooxygenation
WR: 334–395 nm; $\Phi \sim 0.6$ (cf. table below for the exact $\Phi(\lambda)$ values, depending on the excitation wavelength λ) 1.7×10^{-3} M in air-saturated Freon 113 Uvasol Merck
AM: absorbance at 324 nm

λ/nm	$S_{ac}(\lambda) = \Phi(\lambda)\ \varepsilon(324\text{ nm})$/ dm^3 mol^{-1} cm^{-1}	Standard deviation ±	$\Phi(\lambda)$	Standard deviation ±
334	627	8	0.581	0.016
350	642	9	0.595	0.014
365	611	10	0.566	0.015
380	651	10	0.603	0.017
395	616	9	0.571	0.015

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

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

L48: Azo dye ABD [6-{4-[(4-octylphenyl)diazenyl]phenoxy}hexanoic acid] *trans* → *cis* photoisomerization in an assembled monolayer film (Langmuir–Blodgett technique) coated on electrode

WR: 334–405 nm; $\Phi(\lambda) = 0.12 \pm 0.01$ (334 nm), 0.11 ± 0.01 (340 nm), 0.13 ± 0.02 (365 nm), 0.1 ± 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: 2×10^{-4} M $CdCl_2$ subphase $(1.5–2.5) \times 10^{-3}$ 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 (< ± 1.7 %) with different glass substrates. Suitable for < 10^{-8} einstein cm^{-2} s^{-1}; irradiation times of only few seconds.

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

L49: 3,3,8,8-Tetramethyl-1,2,6,7-tetraazaspiro[4.4]nona-1,6-diene photolysis in hexane

For actinometry with circularly *polarized* light. For the determination of molar ellipticity or the degree of circularly polarized light.

WR: 345 nm

AM: CD

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

L50: 1,1'-Azoxynaphthalene [di-(1-naphthyl)diazene oxide, 1,1'-(diazene-1,2-diyl)dinaphthalene oxide]

WR: 350 nm; $\Phi = 0.022$ at 350 nm in 95 % ethanol

AM: absorbance at ≥500 nm

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

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

L51: 2,2',4,4'-Tetraisopropylazobenzene [bis-(2,4-isopropylphenyl)diazene, 1,1'-(diazene-1,2-diyl)*bis* [2,4-bis(2-methylpropyl)benzene]

WR: 350–390 nm; Φ(*trans* → *cis*) = 0.112 ± 0.04 in heptane

AM: absorbance at 365 nm

1. R. Frank and G. Gauglitz. *J. Photochem.* **7**, 355–357 (1977).

L52: Riboflavin irreversible reductive quenching by Na_2EDTA 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

1. S. Lingamurthy, V. Bhanumathi, B. Sethuram. *J. Photochem. Photobiol., A* **68**, 395–399 (1992).

L53: Sodium nitrite/benzoic acid in aqueous solution
WR: 360–380 nm; Φ = 0.001 87 ± 0.000 04 (scavenging product salicylic acid [*p*-hydroxybenzoic acid]), Φ = 0.001 16 ± 0.000 05
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^{-3} M sodium nitrite and 10^{-3} M benzoic acid (OH radical trap) in air-saturated 2.5×10^{-3} M sodium hydrogencarbonate 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)

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

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

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

L55: Tris(2,2'-bipyridine)ruthenium(II) oxidation upon photolysis in the presence of peroxodisulfate
WR: 366, 405, 436 nm; Φ = 1.3 in argon-saturated aqueous solution (1.4×10^{-4} M $Ru(bpy)_3^{2+}$ and 2×10^{-3} M potassium peroxydisulfate [μ-peroxo-bis(trioxysulfate)(2-)], pH ~ 5); S_{ac} = 16 600 $dm^3\ mol^{-1}\ cm^{-1}$
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. F. Bolletta, A. Juris, M. Maestri, D. Sandrini. *Inorg. Chim. Acta* **44**, L175–L176 (1980).
2. H. Görner, H. J. Kuhn, D. Schulte-Frohlinde. *EPA Newslett.* **31**, 13–33 (1987).

L56: Degradation of 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (TAN) by photoproduced hematoporphyrin anion radicals in buffered aqueous solutions. Actinometry in an EPR cavity.
WR: 366, 405, 546 nm, Φ = (4.1 ± 0.2) 10^{-3} in 0.1 M ionic strength amine and borax buffer (pH 9.2), independent of λ
AM: EPR measurement of radical production

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

L57*: 5,12–Diphenylnaphthacene self-sensitized photooxygenation
WR: 405–500 nm; Φ ~ 0.75 (cf. table below for the $\Phi(\lambda)$ values depending on the excitation wavelength λ); in air-saturated Freon 113 Uvasol Merck (1.6×10^{-3} M)
AM: absorbance at 383 nm

λ/nm	$S_{ac}(\lambda) = \Phi(\lambda)\ \varepsilon(383\ nm)/dm^3\ mol^{-1}\ cm^{-1}$	Standard deviation ±	$\Phi(\lambda)$	Standard deviation ±
405	666	12	0.763	0.020
436	662	11	0.759	0.018
450	670	12	0.767	0.018
475	671	12	0.769	0.016
490	657	13	0.753	0.018
500	644	13	0.738	0.018

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

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

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

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

AM: absorbance at about 376 nm

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

L59: Thiourea photooxidation

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

AM: O_2 consumption, manometric

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

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. $\Phi(\lambda) = 0.0351$ (436 nm), 0.0240 (546 nm), 0.0210 (575) nm in toluene. $S_{ac}(\lambda) = 288\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 546 nm

AM: absorbance at 546 nm [$\varepsilon(546\ \mathrm{nm}) = 12\,000\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$]

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 recoloring

1. Private communication by H. G. Heller.
2. For similar compounds, cf. A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. J. Strydom, J. Whittal. *J. Chem. Soc., Perkin Trans. 1* 957–961 (1985).

PP: 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

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

L62: 4-Dicyanomethylene-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran (DCM) [2-(2-{2-[4-(dimethylamino)phenyl]ethen-1-yl}-6-methyl-4*H*-pyran-4-ylidine)propanedinitrile] *trans* → *cis* photoisomerization

WR: 462 nm at continuous and 532 nm at ns **laser** photolysis, $\Phi = 0.28 \pm 0.02$ (in $CHCl_3$), $\Phi = (2.22 \pm 0.05) \times 10^{-2}$ (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

1. J. C. Mialocq, X. Armand, S. Marguet. *J. Photochem. Photobiol., A* **69**, 351–356 (1993).

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

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

AM: absorbance at 429 nm

PP: conversion limit ~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. G. Sauvage. *Ann. Chim.* **2**, 844–873 (1947).
2. H.-D. Brauer, R. Schmidt, G. Gauglitz, S. Hubig. *Photochem. Photobiol.* **37**, 595–598 (1983).
3. A. Acs, R. Schmidt, H.-D. Brauer. *Photochem. Photobiol.* **38**, 527–531 (1983).
4. W. Drews. *Dissertation* Frankfurt (Main) (1980); S. Hubig. *Dissertation* Tübingen (1984).
5. R. Schmidt and H.-D. Brauer. *J. Photochem.* **25**, 489–499 (1984).
6. R. Schmidt. *Ber. Bunsen-Ges. Phys. Chem.* **90**, 813–819 (1986).
7. H.-J. Adick, R. Schmidt, H.-D. Brauer. *J. Photochem. Photobiol., A* **45**, 89–96 (1988).

PP: Actinochrome is no longer commercially available.

L64: Cobalt(III) amines photolysis in aqueous solutions

WR: 488 nm; $\Phi \sim 10^{-4} - 5 \times 10^{-3}$ at 25 °C, pH-dependent

AM: NH_3 release and halide aquation; absorbance at 625 nm

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

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, 8×10^{-5} M MB; cf. table below for the $\Phi(\lambda)$ values as a function of the excitation wavelength λ (halfwidth of monochromatic light: 6 nm), at 22 ± 2 °C; suitable for polychromatic radiation

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

λ/nm	$S(\lambda) = \Phi(\lambda)\,\Delta\varepsilon(405\text{ nm})$/ dm^3 mol^{-1} cm^{-1}	Standard deviation ±	$\Phi(\lambda)$	Standard deviation ±
610	2062	39	0.114	0.003
620	1972	38	0.109	0.003
633*	1918	38	0.106	0.003
654	1918	36	0.106	0.003
670	1919	35	0.106	0.003

*(He–Ne **laser**)

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

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

L66: 7,16-Diphenyldibenzo[*a,o*]perylene (*meso*-diphenylhelianthrene, MDH) photooxygenation, sensitized by 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide [1,7-bis-(1,3,3-trimethylindoline-2-ylidine)heptadienylium iodide] (HITC)

WR: 670–795 nm; $\Phi \sim 0.04$, 1.6×10^{-4} M MDH, 7.2×10^{-5} M HITC in air-saturated $CHCl_3$ solution; cf. table below for the $\Phi(\lambda)$ values as a function of the excitation wavelength λ (half-width of monochromatic light 6 nm); suitable for polychromatic radiation
AM: change in absorbance at 405 nm of endoperoxide, $\Delta\varepsilon(405) = \varepsilon(405, \text{MDH}) - \varepsilon(405, \text{MDHPO})$

λ/nm	$S(\lambda) = \Phi(\lambda)\, \Delta\varepsilon(405\text{ nm})$/ dm^3 mol^{-1} cm^{-1}	Standard deviation ±	$\Phi(\lambda)$	Standard deviation ±
670	818	19	0.0452	0.0017
680	780	18	0.0431	0.0017
685	769	18	0.0425	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

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

Disproved:

L67: Decafluorobenzophenone photoreduction in propan-2-ol
WR: 290–370 nm; $\Phi = 0.60 \pm 0.01$

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

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

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

2.2 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**, **E07**, **E10**] 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 the application of 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 the monitoring of 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

1. R. W. Yip and D. R. Dickinson. *J. Sci. Instrum.* **43**, 758–759 (1966).

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

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

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

1. J. Yguerabide. *Rev. Sci. Instrum.* **39**, 1048–1052 (1968).
2. B. Schaarschmidt. *Z. Naturforsch.* **25b**, 330–331 (1970).

E04: **Physical** light integrator

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

E05: Digital quantum dose integrator with memory

1. J. N. Demas. *Chem. Instrum.* **5**, 283–290 (1973/74).

E06*: Electronically integrating actinometer

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

1. W. Amrein, J. Gloor, K. Schaffner. *Chimia* **28**, 185–188 (1974).
2. H. J. Kuhn. In *Instruments of Science, An Historical Encyclopedia*, R. Bud and D. Warner (Eds.), Vol. 2, p. 15, Garland Encyclopedias in the History of Science, Garland Publ. Inc., New York (1998).

E07*: Electronic actinometer with photomultipliers

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

E08: Luminescent quantum counters

1. D. G. Taylor and J. N. Demas. *Anal. Chem.* **51**, 712–717 (1979); 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

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

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

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

1. H. Baumann, K. Behrmann, H. Jahnke, W. Ortmann, G. Waldmann. *J. Signalaufz.-Mater.* **11**, 385–394 (1983).
2. K. Behrmann, E. Fanghänel, J. Kyziol. *Z. Chem.* **24**, 20–21(1984).

2.3 Absolute measurement of incident photon flux by means of photodiodes

Photodiodes are used for the detection of electromagnetic radiation in the ultraviolet, visible, and infrared 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_{pd}, and the resistance R_{f} of the feedback resistor: $U = i_{\mathrm{pd}}\, R_{\mathrm{f}}$.

Owing 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 (A) per watt of incident radiation, i.e., $S_{\mathrm{pd}}(\lambda)/\mathrm{A\ W^{-1}}$. In actinometry, however, it is important to have diode sensitivities related to photon flux ($q_{n,\mathrm{p}}$) rather than to radiant power. With $E(\lambda) = N_{\mathrm{A}}\, h\, c/\lambda$, one einstein has the energy $E(\lambda)/\mathrm{J} = 0.119\,586\ \mathrm{m}/\lambda$. The needed diode sensitivity is $S_n(\lambda)/(\mathrm{einstein\ s^{-1}\ A^{-1}}) = [S_{\mathrm{pd}}(\lambda)\ E(\lambda)]^{-1}$. By multiplying $S_n(\lambda)$ by the measured photocurrent i_{pd} the desired photon flux/einstein $\mathrm{s^{-1}}$ at wavelength λ 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]. $\Phi_{\mathrm{c}} = 1$ means that the charge of 96 485 Å is produced by the energy $E(\lambda)/\mathrm{J} = 0.119\ 586\ \mathrm{m}/\lambda$ of one einstein of absorbed photons, leading to the maximum possible sensitivity $S_{\mathrm{pd}}(\lambda)/\mathrm{A\ W^{-1}} = 8.066 \times 10^5\ \lambda/\mathrm{m}$. 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 $S_{\mathrm{pd}}(\lambda)$ 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, with a constant Φ_{c} from 1100 to 2700 nm according to the data sheets of the manufacturer [4].

Some mass-produced Si photodiodes show direct proportionality of $S_{\mathrm{pd}}(\lambda)$ with λ in a broad range of the visible spectrum, indicating a constant value of Φ_{c} (e.g., Hamamatsu S2387). The relative $S_{\mathrm{pd}}(\lambda)$ data plotted vs. λ in Fig. 1 have been extracted from the S2387 data sheet (<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 Fig. 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 Fig. 1. The fit follows the relation $S'_{\mathrm{pd}}(\lambda)/\ \mathrm{A\ W^{-1}} = 5.82 \times 10^5\ \lambda/\mathrm{m}$. As shown above, $S_{\mathrm{pd}}(\lambda)/\mathrm{A\ W^{-1}} = 8.066 \times 10^5\ \lambda/\mathrm{m}$ holds true in the absence of reflection loss for $\Phi_{\mathrm{c}} = 1$. Therefore, the mean apparent quantum yield of charge carrier formation of the S2387 diode including reflection loss amounts to $\Phi_{\mathrm{c}} = 0.72 \pm 0.05$ between 450 and 1000 nm. Thus, the charge of 72 180 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 $S_n(\lambda)/\mathrm{einstein\ s^{-1}A^{-1}} = 1.44 \times 10^{-5}$ between 450 and 1000 nm.

Therefore, this cheap Si-photodiode may be used as a polychromatic quantum counter of constant sensitivity $S_n(\lambda)/\mathrm{einstein\ s^{-1}A^{-1}} = 1.44 \times 10^{-5}$ 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.

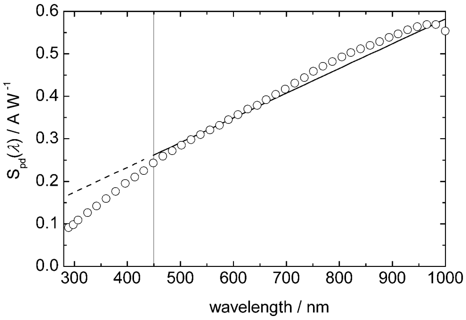

Fig. 1

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

References to Section 2.3:

1. Photochemical set-up: W. Drews, R. Schmidt, H.-D. Brauer. *J. Photochem.* **6**, 391–403 (1976/77).
2. Calibration of chemical actinometers: H.-D. Brauer and R. Schmidt. *Photochem. Photobiol.* **37**, 587–591 (1983); A. Acs, R. Schmidt, H.-D. Brauer. *Photochem. Photobiol.* **38**, 527–531 (1983).
3. Quantum yield of electron-hole-pair formation of a Si photodiode: J. Geis, E. F. Zalewski, A. R. Schaefer. *Appl. Opt.* **19**, 3795–3799 (1980).
4. Determination of the quantum yield of the 1940 nm b → a emission of singlet oxygen: R. Schmidt and M. Bodesheim. *J. Phys. Chem.* **99**, 15919–15924 (1995).
5. Spectral sensitivity of other semiconductor devices (Si, Ge, InAs, HgCdTe): Infrared Detector 1998, EG & G Optoelectronics, Judson, Laser Components GmbH, URL: <http://www.laser-components.de>.

3. STANDARD LIQUID-PHASE ACTINOMETRIC PROCEDURES

(For references and more data, cf. Section 2.1.3, above.)

L02*: *cis*-Cyclooctene *cis* → *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 (2×10^{-2} M, total absorption) containing nonane as a GC standard is 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 relatively 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 photons N_{p} absorbed per sample volume V and unit time t, is calculated from

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

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 ($[trans]_\infty/[cis]_\infty \sim 1$). $[cis]_\infty/[cis]_0$ 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 2.1.3.

L03*: Ethanol photolysis (Farkas actinometer)
(submitted by C. von Sonntag 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 1 min excitation with a photon flux (number basis) 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 [dioxouranium(VI) oxalate] photolysis
(submitted by D. F. Eaton and 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.

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

After irradiation, the nonreacted $C_2O_4^{-2}$ is titrated with a solution of Ce(IV) sulfate, following the reaction:

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

Preparation of solutions: 0.42478 g uranyl sulfate (UO_2SO_4) and 0.672 62 g disodium oxalate ($Na_2C_2O_4$, primary standard grade) are dissolved in 0.1 M H_2SO_4 and diluted to 1.0 dm^3 in the dark. The solution is 5.004×10^{-3} M in oxalate dianion and 1.011×10^{-3} M in uranyl ion. Store in the dark. Ce(IV) 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 M 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 1 M 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. 0.1 M H_2SO_4 in a 1.0-cm cell. The decadic molar absorption coefficient of Ce(IV) at 320 nm is $\varepsilon(320\ \text{nm}) = 5.41 \times 10^3\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$. 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 Ce(IV) 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 *flask* 2. 1.0 cm^3 of the standard Ce(IV) solution and 1.0 cm^3 H_2SO_4 (1 M) are added, and the solution is brought to the mark with water. Both irradiated samples and nonirradiated 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, amount basis, $q_{n,\text{p}}$/einstein s^{-1} entering the sample cell is given by:

$$q_{n,\text{p}} = \frac{V_{irrad}\ \Delta A\ V_{flask2}}{2\ \Phi(\lambda)\ f\ \varepsilon(320\ \text{nm})\ V_{\text{aliq}}\ l\ t}$$

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 = irradiation time; Φ = 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 nm) = molar absorption coefficient of Ce(IV). The factor 2 in the denominator results from the stoichiometric factor in the titration reaction. ΔA(320 nm) is the absorbance difference between sample and nonirradiated blank, and l/cm is the pathlength.

The oxalate photodecomposition quantum yields [$\Phi(\lambda)$] are:

λ/nm	$\Phi(\lambda)$	λ/nm	$\Phi(\lambda)$	λ/nm	$\Phi(\lambda)$
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 of Ce(IV) at the analyzing 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 nonirradiated 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; $\Phi(trans \rightarrow cis) = 0.14$; $\Phi(cis \rightarrow trans) = 0.48$; $S_{ac} = 130\text{–}3900\ \mathrm{mol^{-1}\ dm^3\ cm^{-1}}$

Wavelength range 245–266 nm: The solution is preirradiated at 313 nm. The actinometry (as above) then starts at the photostationary state [A(358 nm) ~ 0.30] and the final value should be A(358 nm) < 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 nm) ca. 1 is recommended. Each irradiation period should cause a change in A(358 nm) 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 preirradiated 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 nm) is the change in absorbance at 358 nm and t/s = irradiation time. The factors $F(\lambda)$ are given in the table below. Thus, the photon irradiance (in amount basis) entering the sample cell is $E_\mathrm{P}/\mathrm{einstein\ cm^{-2}\ s^{-1}} = F(\lambda)\ \Delta A(358\ \mathrm{nm})/t$.

λ/nm	$F(\lambda)$/ 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 ($q_{n,\mathrm{p}}$/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 $E_\mathrm{P} = \frac{\tau}{\boldsymbol{C}\,t}$, with $\boldsymbol{C} = [\Phi(trans \rightarrow cis)\ \varepsilon(\lambda,trans) + \Phi(cis \rightarrow trans)\ \varepsilon(\lambda,cis)]\ 1000$, the pseudo total quantum yield and ε at the irradiation wavelength. $\boldsymbol{C}$ 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. The lifetime τ is taken from calibration graphs of the time-dependent absorbance vs. t.

L31*: Iron(III) potassium oxalate trihydrate [potassium tris(oxalato)ferrate(III) trihydrate] $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$), photoreduction (Hatchard–Parker actinometer, commonly called ferrioxalate actinometer)
(submitted by G. Gauglitz and S. Hubig)
WR: 250–500 nm; $\Phi = 1.25 - 0.9$; $S_{ac} = 13\,900 - 9990\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$

All procedures should be done under red safe-light. Green crystals of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ are prepared by mixing 3 vol 1.5 M $K_2C_2O_4$ 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 (≥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_2SO_4 (0.5 M) 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. For example, 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 $NaC_2H_5CO_2$, 10 cm^3 conc. H_2SO_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 color development is achieved, and the absorbance difference between the two samples is measured at 510 nm [optical pathlength l = 1 cm, ε(510 nm) = 11 100 $dm^3\ mol^{-1}\ cm^{-1}$]. A(510 nm) should be within the range 0.4–1.8. Conversion should not exceed 5 %. The photon flux, amount basis, $q_{n,\mathrm{p}}$/einstein s^{-1} , entering the sample cell is given by (in coherent SI units):

$$q_{n,\mathrm{p}} = \frac{\Delta A \ \ V_1 \ V_3}{\Phi(\lambda) \ \varepsilon(510\,\mathrm{nm}) \ V_2 \ \ l \ t}$$

with t = irradiation time. 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: Owing to its high S_{ac}-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: Aberchrome 540 [(*E*)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)succinic anhydride] ⇄ Aberchrome 540P [7,7a-dihydro-2,4,7,7,7a-pentamethylbenzo[*b*]furan-5,6-dicarboxylic anhydride]
(submitted by H. G. Heller)
WR: 310–375 nm; Φ = 0.2; S_{ac} = 1640 $dm^3\ mol^{-1}\ cm^{-1}$

A ca. 5×10^{-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 l = 1 cm cell and mixing, the absorbance at 494 nm is measured. The increase in ΔA(494 nm) enables the calculation of the photon flux, amount basis, $q_{n,\mathrm{p}}$/einstein s^{-1}, entering the sample cell with

$$q_{n,\mathrm{p}} = \frac{\Delta A(494\,\mathrm{nm}) \ \ V}{\Phi \ \ \varepsilon(494\,\mathrm{nm}) \ \ l \ \ t}$$

where V = irradiated volume, Φ = 0.20 from 310–375 nm, ε(494 nm) = 8200 $dm^3\ mol^{-1}\ cm^{-1}$, t = time. For recent quantum yields cf. [10e]. The colored form is reversed with white light.
PP: Reuse of the actinometer solution after photoreversion is strongly discouraged.
Aberchrome 540 is no longer commercially available.

L47*: 9,10-Dimethylanthracene self-sensitized photooxygenation
(submitted by R. Schmidt)
WR: 334–395 nm; $\Phi = 0.583 \pm 0.15$; $S_{ac} = (629 \pm 17)$ 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 $\varepsilon(324 \text{ nm}) = 1080$ mol^{-1} dm^3 cm^{-1}) of initial absorbance $A(324 \text{ nm}) = 1.8$ (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, amount basis, $q_{n,\mathrm{p}}$/einstein s^{-1}, entering the sample cell is calculated by using the absolute value of the absorbance decrease $\Delta A(324 \text{ nm})$ and the following equation

$$q_{n,\mathrm{p}} = \frac{\Delta A(324 \text{ nm}) \ V}{\Phi(\lambda)\ \varepsilon(324 \text{ nm}) \ t \ l}$$

with t = irradiation time, V = volume of the solution (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 a mean value $\Phi(\lambda)\ \varepsilon(324 \text{ nm}) = (629 \pm 17)$ dm^3 mol^{-1} cm^{-1} and $\Phi(\lambda) = 0.583 \pm 0.015$. Values of $S_{ac} = \Phi(\lambda)\ \varepsilon(324 \text{ nm})$ at particular irradiation wavelengths are given under **L47*** in Section 2.1.3.

L57*: 5,12-Diphenylnaphthacene self-sensitized photooxygenation
(submitted by R. Schmidt)
WR: 405–500 nm; $\Phi = 0.758 \pm 0.16$; $S_{ac} = (662 \pm 13)$ 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 $\varepsilon(383 \text{ nm}) = 873$ dm^3 mol^{-1} cm^{-1}) of initial absorbance $A(383 \text{ nm}) = 1.4$ (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, amount basis, $q_{n,\mathrm{p}}$/einstein s^{-1}, entering the sample cell is calculated by using the absolute value of the absorbance decrease $\Delta A(383 \text{ nm})$ upon irradiation and the following equation

$$q_{n,\mathrm{p}} = \frac{\Delta A(383 \text{nm}) \ V}{\Phi(\lambda)\ \varepsilon(383 \text{ nm}) \ l \ t}$$

with t = irradiation time, V = volume of the solution (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 a mean value $S_{ac} = \Phi(\lambda)\ \varepsilon(383 \text{ nm}) = (662 \pm 13)$ dm^3 mol^{-1} cm^{-1} and $\Phi(\lambda) = 0.758 \pm 0.016$. Values of $S_{ac} = \Phi(\lambda)\ \varepsilon(383 \text{ nm})$ at particular irradiation wavelengths are given under **L57*** in Section 2.1.3.

APPENDIX

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

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