

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION

COMMISSION ON PHOTOCHEMISTRY*

**RECOMMENDED STANDARDS FOR
REPORTING PHOTOCHEMICAL DATA**

(Recommendations 1983)

Prepared for publication by

A. A. LAMOLA¹ and M. S. WRIGHTON²

¹Bell Laboratories, Murray Hill, New Jersey 07974, USA

²Massachusetts Institute of Technology, Cambridge, Mass. 02139, USA

*Membership of the Commission during which the report was prepared (1979-83) was as follows:

Chairman: 1979-81 K. SCHAFFNER (FRG); 1981-83 F. C. DE SCHRYVER (Belgium); *Secretary:* 1979-81 F. C. DE SCHRYVER (Belgium); 1981-83 A. A. LAMOLA (USA); *Members:* S. E. BRASLAVSKY (FRG, Associate 1981-83); D. F. EATON (USA, Associate 1981-83); Z. R. GRABOWSKI (Poland, Titular 1979-81); C. HÉLÈNE (France, Associate 1979-81); K. N. HOUK (USA, Titular 1979-83); H. IWAMURA (Japan, Associate 1979-83); M. G. KUZMIN (USSR, Associate 1981-83); J. MICHL (USA, Associate 1979-81, Titular 1981-83); M. OTTOLENGHI (Israel, Associate 1979-81); C. SANDORFY (Canada, Associate 1979-83); K. TOKUMARU (Japan, Titular 1979-83); D. W. TURNER (UK, Associate 1979-83); D. G. WHITTEN (USA, Associate 1979-81); U. P. WILD (Switzerland, Associate 1979-81); F. WILKINSON (UK, Associate 1981-83); M. S. WRIGHTON (USA, Titular 1979-83); *National Representatives:* A. M. OSMAN (Arab Rep. of Egypt); O. P. STRAUSZ (Canada); K. LEMPert (Hungary); J. W. VERHOEVEN (Netherlands).

RECOMMENDED STANDARDS FOR REPORTING PHOTOCHEMICAL DATA

The assessment or reinterpretation of experimental results requires that the reports contain sufficient information about experimental procedures and conditions. This is, of course, especially important in order to allow repetition of experiments by other investigators. While some experimental practices are so standard or common as to be assumed, many are not. It is therefore, important that the crucial experimental parameters be included in published reports.

The purpose of this document is to recommend a comprehensive set of experimental parameters and data manipulation methods that should be reported in published accounts of photochemical investigations and attendant spectroscopic studies.

It should be understood that quantitative data concerning all the parameters recommended for inclusion in a report may not be required. For example, references to instrumental settings or operating conditions may be sufficient. In other cases limiting values may suffice, e.g., "the pulse width was less than $1\mu\text{s}$."

I. Photochemical Reactions

A. Conditions

1. Reactants and addends (sensitizers, quenchers, buffers, etc.)
 - a. Purities and methods of purification
 - b. Concentrations or partial pressures
 - c. Relevant spectral properties
2. Solvent, including method of purification
3. Temperature
4. Gaseous atmosphere and methods of manipulation (degassing method, composition of flushing gases)
5. Description of reaction vessel
 - a. Material, e.g., type of glass
 - b. Geometry
 - c. Relevant optical properties (transmission cutoff wavelength, etc.)
 - d. Additional equipment (stirrer, etc.)
6. Exciting radiation
 - a. Spectrum
 - i. Excitation source and condition of operation
 - ii. Dispersing or filtering elements (bandpass)
 - iii. Linewidth (for laser lines)
 - b. Intensity (radiant flux; fluence rate) at sample ($\text{Jm}^{-2}\text{s}^{-1}$; photons $\text{m}^{-2}\text{s}^{-1}$) and area irradiated

c. Irradiation dose (fluence) (Jm^{-2})

- i. If continuous irradiation, state radiant flux (intensity) and time.
- ii. If intermittent irradiation, state radiant flux, cycle duration and number of cycles.
- iii. If pulsed irradiation, state dose (fluence) per pulse, pulse width, repetition rate, number of pulses.

B. Quantum Yields

1. Definition of yield reported:

$$\Phi = \frac{\text{number of moles transformed (reacted, produced, etc.) in a process}}{\text{number of moles of photons absorbed}}$$

In the classical definition, the substance absorbing the exciting radiation is identical to that undergoing the photochemical (or photophysical) process of interest. In a complicated reaction mixture more than one substance, and perhaps not the reactant of interest, may absorb the excitation radiation. The reference photon absorption (the denominator in the equation above) must then be clearly defined. For example, in a sensitized reaction a quantum yield based upon the number of substrate molecules reacted per photon absorbed by the sensitizer may be defined. When a clear definition cannot be made, it is preferred that the term "apparent quantum yield" be used. It may not be possible in some cases, for example, in biological systems, to determine the absorbed dose. An experimentally determined efficiency based upon the exposed dose may be defined. Such a quantity should not be called a quantum yield. It is, of course, commonly possible to determine the efficiencies of individual primary processes and to define a quantum yield based upon the number of occurrences of the process of interest per molecule in the excited state which may undergo that process. **THE AUTHOR SHOULD CLEARLY INDICATE WHAT YIELD IS BEING REPORTED.**

2. "Units"

Should be reported as a fraction and not as a percent (e.g., 0.5 rather than 50%)

3. Conditions

- a. See section I.A.
- b. Other necessary data include:
 - i. Wavelength and bandwidth, or spectrum of exciting radiation
 - ii. Intensity (radiant flux) of exciting radiation
 - iii. Actinometric or dosimetric methods
 - iv. Computational methods if complex (corrections for absorption of radiation by substances other than reagent of interest)
 - v. Error estimate and number of determinations

C. Chemical Yields

1. Definition

The yield should be clearly defined: Isolated yield refers to material that is actually isolated. Detected yield refers to quantity of material that can be detected by some analytical method, e.g., gas chromatography

2. Conditions
See section I.A.
3. Variation of yield
 - a. Dependence upon intensity (radiant flux) of exciting radiation
 - b. Dependence upon wavelength of exciting radiation
 - c. Dependence upon concentrations of relevant substances
 - d. Dependence upon conversion (extent of reaction)

D. Kinetics

1. Conditions
See section I.A.
2. Data display
Data points and error limits should be displayed in plots
3. Analysis
 - a. Model or mechanistic scheme upon which the analysis of kinetics is based should be clearly indicated
 - b. Fitting methods used should be reported
 - c. Statistics and error analysis should be included

II. Absorption Spectroscopy

A. Display

1. Energy or wavelength on abscissa (x-axis)
A display linear in energy is preferred with the wavenumber ($\tilde{\nu}$) (cm^{-1}) the preferred scale. The preferred scale direction is "red to right," i.e., decreasing energy or increasing wavelength goes left to right. The measure of wavelength is nm (nanometer).
2. Measure of absorptivity on ordinate (y-axis)
Options are:
 - a. ϵ , molar absorption coefficient (molar absorptivity) ($\text{m}^2\text{mol}^{-1}$ is the preferred unit; $\text{l mol}^{-1}\text{cm}^{-1}$ has been commonly used. Note that $\text{m}^2\text{mol}^{-1} = 10 \text{l mol}^{-1}\text{cm}^{-1}$. SPECIFY UNITS).
 - b. Absorbance (A) (internal absorbance or decadic internal absorption) ($\log_{10}T^{-1}$, where T = internal transmittance or fractional transmission). This refers specifically to the attenuation of radiation by absorption within the specimen.
 - c. Attenuance (\tilde{A}) ($\log_{10}\tau^{-1}$ where τ is the transmittance)
This refers specifically to the attenuation of transmitted radiation by all mechanisms including scatter.
3. If spectrum was measured point by point, the data points and error limits should be displayed.

B. Conditions

1. See section I.A.
2. Instrumentation should be described.
3. Spectral resolution should be defined.
4. Photometric errors and errors due to stray, scattered and emitted radiation should be assessed.

C. Transient absorption and flash kinetics

1. See sections I.A., I.D., and II.A.3.

2. Instrumentation should be described
 - a. Pulse width (and pulse rate if applicable)
 - b. Time resolution
 - c. Wavelengths and bandwidths of exciting and monitoring radiation beams
 - d. Intensities of exciting and monitoring radiation beams (energy per pulse for laser or flash sources)
 - e. Geometry, cross-sections, etc. of exciting and monitoring radiation beams
 - f. Relative polarizations of exciting and monitoring radiation beams (laser sources)
 3. Deconvolution method
- D. Action spectra
1. See sections I.A. and II.A.
 2. Intensity (radiant flux) dependence
 3. Concentration dependence (extrapolation to "zero" concentration for comparison with absorption spectra)
- III. Luminescence Spectroscopy
- A. Display
1. Energy or wavelength on abscissa (a linear energy scale is preferred, see section II.A.1.). (If a spectrum on a linear wavelength scale is to be transformed to one on a linear energy scale remember that $d\nu = \lambda^{-2}d\lambda$.)
 2. Relative measure of photon flux on ordinate
 - a. If point by point, show points
 - b. When comparing spectra, normalize integrated intensities (radiant fluxes) to reflect relative luminescence yields. (It is best to use a linear energy scale for the abscissa.)
 - c. State what corrections were applied to the experimental spectrum (i.e., corrections for instrumental spectral response, dispersion of solvent, refractive index, polarization, stray and scattered excitation radiation, bleaching, etc.).
 3. Define time gate
 - a. "Total" emission vs "time-resolved" emission
 - b. Time gate for time-resolved fluorescence
- B. Conditions
1. See section I.A.
 2. Description of instrument
 3. Wavelength and bandwidth of exciting radiation
 4. Intensity (radiant flux) of exciting radiation
 5. Appropriate description of exciting radiation intensity-time profile
 6. Polarization of exciting radiation
 7. Method of calibration of excitation and emission wavelength determination
 8. Description of excitation spectrum

- C. Kinetics (luminescence decay)
 - 1. See sections I.D. and II.C.
 - 2. Emission wavelength and bandwidth
 - 3. Methods used for deconvolution and analysis
- D. Luminescence yield
 - 1. See sections I.A., I.B., and III.B.
 - 2. Reference substance defined if relative measure (include yield assumed for reference substance)
 - 3. Dosimetry defined if absolute measure
 - 4. Dependence upon wavelength of exciting radiation
 - 5. Concentration dependence
 - 6. Dependence upon intensity (radiant flux) of exciting radiation
 - 7. State what corrections were made for reabsorption effects, etc.
- E. Excitation spectra
 - 1. Define geometry
 - 2. Absorbance of sample
 - 3. Emission wavelength and bandwidth
 - 4. State what corrections were made for photon flux variations of spectrum of exciting radiation.
 - 5. State what corrections were made for extraneous absorbance, etc.
- F. Chemiluminescence
 - 1. Conditions, see sections I.A.1 to I.A.5
 - 2. Spectra
 - a. Instrumentation
 - b. State what corrections were made for nonconstant reaction rate during spectral scan.
 - 3. Intensity (radiation flux) and Quantum Yield
 - a. Reaction rate dependence
 - b. Dosimetry (calibration)

IV. Abstract

Because the abstract of a published report is essentially what is reprinted by abstracting services, etc., it is important for effective data retrieval that quantitative data for important findings be placed in the abstract. Such data might include quantum yields, rate constants, equilibrium constants, and spectral features such as wavelengths of maxima.