Designation: E 896 – 92 (Reapproved 2005)

Standard Test Method for Conducting Aqueous Direct Photolysis Tests[1]

This standard is issued under the fixed designation E 896; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes procedures for obtaining information on direct photolysis rates, quantum yields, and phototransformation products of materials in an aqueous environment. Laboratory testing procedures designed to provide estimates of environmental rates of photolysis are described.

1.2 A three-tiered approach is described. The testing procedures are designed to provide basic and easily obtainable information in the first tier. More detailed and costly experiments are proposed in the second and third tiers. This approach is thought to be more scientific and cost-effective than one which provides for no sequential assessment. It is not within the scope of this test method to provide decision points to move from one tier to the next. The degree of testing should be decided as part of an overall exposure assessment in which the importance of photolysis is weighed with respect to other transformation routes.

1.3 These procedures are designed to be applicable to all types of materials. However, tests on formulations and commercial products that are complex mixtures of materials with diverse physical and chemical properties may require isolation of individual compounds prior to testing to eliminate indirect photochemical reactions. With slight modification, these procedures should meet the needs of most investigators.

1.4 In developing this test method an attempt was made to balance the needs and costs against the scientific considerations and reliability of results. Major considerations were: (*1*) that the procedures generate precise, accurate, and environmentally relevant data, and (*2*) that the procedural requirements be as flexible as possible without destroying this integrity of the data and the ability to compare interlaboratory results.

1.5 Since all details are not covered in this test method, successful execution of the described tests will require some training or experience in the area of photolysis. Familiarity with the material in the references is essential. Detailed descriptions on conducting similar test procedures have been published by the U.S. Environmental Protection Agency (**1, 2**).[2]

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 1193 Specification for Reagent Water

E 131 Terminology Relating to Molecular Spectroscopy

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *Beer-Lambert law*—the law that states that the absorbance of a homogeneous sample is directly proportional to the concentration of the absorbing material and to the thickness of the sample in the optical path.

3.1.2 *direct photolysis*—direct absorption of light by a molecule followed by a reaction that converts the parent molecule into one or more products. These transformations depend on adsorption of energy (photons) in the ultraviolet-visible spectrum. The rate of transformation depends upon the absorption of photons, light intensity (photon flux), and quantum yield.

3.1.3 *first-order rate equation*—an equation that describes a reaction rate that is linearly dependent on the concentration. The half-life of the reaction is independent of the concentration. The photolysis rate equation shown in 3.1.10 is a first-order equation.

3.1.4 *Grotthus-Draper law* (first law of photochemistry)—the law that states that only light absorbed by a molecule is responsible for a reaction.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this test method.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.5 *half-life* ($t_{1/2}$)—the time required for half of the parent material to react. For a first-order rate equation, $t_{1/2} = (0.693/K)$.

3.1.6 *indirect photolysis*—absorption of light by a "sensitizer" molecule followed by energy transfer to a molecule of another species that does not adsorb light in the same region. Therefore a molecule that does not directly absorb light can undergo reaction as a result of energy transfer from a sensitizer molecule (**3-7**). Other mechanisms besides energy transfer can cause accelerated reaction in natural water. These include hydrogen abstraction by the sensitizer, electron transfer, and oxidations mediated by photochemically generated species like singlet oxygen or free radicals (**7-9**).

3.1.7 *molar absorptivity* (ϵ)—the product of the absorptivity, *a*, and the molecular weight of the substance. (Terminology E 131).

3.1.8 *nanometre (nm)*—1 × 10–9 m.

3.1.9 *photolysis rate* ($-d[P]/dt$)—the disappearance of parent material per unit of time.

3.1.10 *photolysis rate equation* ($-d[P]/dt) = K[P]$)—an equation that describes the rate of phototransformation as the product of the rate constant (K) and the concentration of the parent material. This equation is applicable to most environmental situations in which P absorbs only a small fraction of the light at any given wavelength.

3.1.11 *phototransformation (photolysis)*—a light-induced change in the structure of a molecule.

3.1.12 *quantum theory*—energy transfers between light and matter occur only in discrete amounts of energy called quanta.

3.1.13 *reaction quantum yield* (ϕ_r)—For any given parent material (P) that is transformed into product B by the reaction $P + hv \rightarrow B$, the quantum yield (ϕ_r) is defined as the molecules of P reacted per unit volume per unit time divided by the quanta of light absorbed by P per unit volume per unit time.

3.1.14 *reagent water*—Type II reagent water in accordance with Specification D 1193.

3.1.15 *Stark-Einstein law* (second law of photochemistry)—the law that states that one molecule is activated for each light quantum (photon) absorbed in a system. A corollary to this law is: the sum of the primary quantum yields of all the processes that deactivate an excited molecule equals unity.

4. Summary of Test Method

4.1 Test procedures are described that can be used to measure rates of aqueous photolysis, rate constants, and reaction quantum yields for most materials. Test methods for using these data to predict environmental aqueous photolysis rates are discussed with reference to specific literature citations.

4.2 A sequential testing approach is described that consists of three tiers of testing. Tier I tests determine the potential for phototransformation for a material. Tier II tests determine rates of photolysis, half lives, and quantum yields. Tests in Tier III identify phototransformation products.

4.3 The photolysis tests in this test method are presented as a guide that can be used to estimate environmental phototransformation.

5. Significance and Use

5.1 For some materials, photolysis is one of the most significant means of transformation in the environment. These photolysis tests provide a means of estimating rates of natural phototransformation of a material in the environment. Determination of phototransformation products may provide insight into possible effects of the material on the environment and suggest areas for ecological effects tests. Photolysis tests assist in the decision-making process necessary for an exposure assessment program.

6. Hazards

6.1 Special precautions must be taken to prevent exposure of laboratory personnel to ultraviolet light in order to avoid damage to the retina of the eye and possibly to skin. The ultraviolet photoreaction system should be suitably shielded in a laboratory hood or other enclosure. Laboratory personnel working with the system should wear appropriate safety glasses or goggles at all times.

7. Sequential Testing Approach

7.1 *Tier I*—The purpose of Tier I is to classify the environmental phototransformation behavior of a material in water that absorbs light of 290 nm or higher wavelength. An aqueous solution of the material is prepared and exposed to light. After a specified length of time, the amount of the parent material remaining in solution is determined. Tier I tests can be conducted with either a laboratory light source or sunlight.

7.2 *Tier II*—The purpose of Tier II is to estimate the environmental photolysis rate of the test material. This can be done using either sunlight or laboratory photochemical reactors. In the first approach, an aqueous solution of the material is exposed to sunlight and its concentration is monitored as a function of time. The half-life is estimated from a semi-log plot of concentration versus time. In the photochemical reactor method, the quantum yield of the reaction is determined by exposing the compound to monochromatic light of measured intensity. The environmental half-life is then estimated using the quantum yield and adsorption spectrum in conjunction with a computer program to estimate the solar irradiance.

7.3 *Tier III*—The purpose of Tier III is to determine phototransformation products. This level of testing is recommended when the photolysis rate data, compared with rates of other environmental transformation processes in the framework of a mathematical model, indicates that photolysis is an important pathway under environmental conditions. The time, expense, and equipment required to complete these tests dictate that they be conducted only when necessary and then in the later stages of systematic exposure assessment program for the material.

7.4 The degree of testing beyond Tier I should be based on the following:

7.4.1 The relative importance of photolysis with respect to other transformation routes (based on information from Tier I tests).

7.4.2 Results of ecological effects tests.

7.4.3 Estimated environmental concentration.

7.4.4 Route of entry into the aquatic environment.

7.4.5 Proposed use and volume of production.

8. Experimental Considerations

8.1 Wavelength distribution and incident light intensity are the most important factors affecting a material's rate of photolysis. Using sunlight as the light source is the most straightforward way to duplicate the spectrum that the compound will be exposed to in the environment. However, sunlight can be quite variable in intensity, depending on season, atmospheric conditions, and geographic location. Laboratory light sources can be much more stable, but great care must be taken to ensure that the light the test material is exposed to closely resembles the wavelength distribution of sunlight at the earth's surface. The wavelengths that produce most photochemical reactions fall in the ultraviolet range (40 to 400 nm) (**10**). However, essentially all UV radiation below 290 nm is absorbed by the upper atmosphere and does not reach the earth's surface (**11**).

8.2 A variety of methods have been used to expose materials to sunlight (**12**)**.** Several considerations are recommended:

8.2.1 Solutions should be exposed to sunlight in a location free of reflections and shadows during the entire daylight period.

8.2.2 Reaction vessels should be mounted over a black background to minimize reflection.

8.2.3 Reaction vessels constructed of quartz or high-silica glass are highly recommended. Borosilicate glass may be used but photolysis rates may be substantially reduced because of absorption of lower wavelengths (320 to 290 nm) by the glass.

8.2.4 The reaction vessel should be tightly sealed with minimal headspace to prevent evaporation and contamination. The vessel may be inverted to further reduce volatility losses.

8.2.5 Reference materials of various photochemical half-lives should be included in all sunlight screening tests (see Table 1). To avoid the possibility of complicating interactions, each solution should contain only a single test material.

8.2.6 The use of a transparent thermostatted housing may be necessary if sunlight exposures are used for photolysis rate determinations. The effects of any housing should be investigated with chemical actinometers or reference chemicals (see 8.7).

8.3 Laboratory photochemical equipment may be used for Tier I screening and Tier II photochemical rate measurements with appropriate limitations.

TABLE 1 Suggested Reference Materials for Use in Determining Photolysis Rates

Compound	Half Life in Sunlight^{A}	ϕ_r, λ(nm)	Ref.
1. 3,3′-Dichlorobenzidine	1 to 2 min	0.43, 254	39
	<6 h^{B}	0.053, 313	40
2. 3,4-Dichloroaniline	5 to 15 days	0.0055, 313	41
3. Carbaryl	10 to 20 days	0.00017, 313	42
4. Methyl parathion			
5. ρ-Nitroanisole Actinometer			44, 45
6. ρ-Nitroacetophenone Actinometer			44, 45

^{A} Ranges are used to accommodate seasonal and geographic changes in sunlight intensity. References for compounds 3 and 4 contain information on photolysis half-life versus time of year.

^{B} See results of round-robin experiment in Table 2.

8.3.1 The light source and filter system should provide light of constant intensity and wavelength distribution. For Tier I screening, the source and filters should be carefully selected to closely resemble sunlight in wavelength and intensity and to eliminate wavelengths less than 290 nm. For best results, the laboratory light source should be compared to sunlight, using a reference material having an absorption spectrum similar to that of the test material.

8.3.2 A number of types of reactors and light sources have been used. Xenon arc lamps generally give a good simulation of solar radiation, especially in the ultraviolet region. Manufactured, self-contained units utilizing a linear parabolic chamber with a xenon arc lamp mounted at the focal line have recently been introduced (**13**).[4] The spectral output of the xenon arc is relatively constant throughout the life of the lamp. Filters can be installed to eliminate low wavelength UV (<290). The unit is open on the bottom of the test chamber to allow any sample configuration. The reactor described by Crosby (**14**), has a cylindrical annular configuration with a fluorescent blacklight in the center as a light source. In the reactor used by Plimmer et al (**15**) and Plimmer (**16**), a circular bank of low-pressure mercury arc or fluorescent lamps surround the reaction cells placed in the center cavity. The merry-go-round apparatus developed by Moses and co-workers (**17**) consists of a turntable that rotates around a light source. It is especially convenient because it can be used to irradiate a number of samples at one time and filters can be placed between the samples and light source. In optical bench systems, light from a source mounted at one end of the bench passes through a collimator and appropriate filters into a reaction cell mounted at the other end. Various quartz and borosilicate immersion-well apparatus have been employed with a number of lamps (**18-22**). Several authors have presented a comprehensive summary of photochemical equipment and components (**23-25**).

8.4 Since the photochemical reactivity of materials in water and organic solvents may be quite different, water should be used as the sole or major solvent if environmentally relevant data are to be obtained. Because of the low solubility of many organic materials, the use of a minimal amount (1 % or less) of a co-solvent may be necessary from the handling and analysis standpoint. A study suggests that acetronitrile is the most suitable co-solvent. The ideal co-solvent should not participate in the photochemical processes. Many co-solvent candidates (for example, ethanol, methanol, dioxane, acetone) besides enhancing the solubility of the test material, also act either as hydrogen donors in free radical reactions or as photosensitizers and are therefore unsuitable.

8.5 *Test Water:*

8.5.1 The presence of substances such as humic and fulvic acids and riboflavin in natural waters can affect the rates of photolysis by acting either as light absorbers or photosensitizers (**26-28**). For this test method water solutions should be prepared using reagent water.

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[4] Available from Heraeus DSET Laboratories, Inc., 45601 N. 47th Ave., Phoenix, AZ 85027-7042.

8.5.2 Since the presence or absence of oxygen can have an effect on the material and photochemical processes that occur in water, standardization with respect to this parameter is desirable. Since most environmental areas that receive sunlight are aerobic in nature, air-saturated water should be used at the start of the test.

8.5.3 All water should be sterilized to deter biodegradation by filtering through a sterile 0.22-μm filter.

8.6 Most materials exist in the aqueous environment below their water solubility. Test concentrations that approximate naturally occurring levels should be used. This is usually below 1 mg/L. Determination of transformation products may require concentrations in excess of 1 mg/L to have sufficient material for analytical determinations. However, concentrations should be kept as low as possible to minimize reactions that would not occur at environmental concentrations. Zepp et al (**29**) have shown that different transformation products may be obtained when wide ranges of initial concentrations are used.

8.7 The rates of photochemical reactions are not thought to be affected to any appreciable extent by changes in temperature. However, reactions subsequent to photoactivation may be greatly affected by temperature. For purposes of standardization, all photolysis tests should be conducted in liquid solutions at temperatures less than 35°C. The reaction temperature range should be recorded. Control solutions (see 8.11) should be maintained at the same temperature as the test solutions.

8.8 Since pH or hydrogen ion concentration has been demonstrated to influence the rate of photochemical reactions as well as the type of products (**30, 31**), all tests should be conducted in the environmentally significant pH range (pH 5 to 9). Photolysis of ionizable materials can exhibit marked pH effects that are attributable to changes in speciation. If different species are present in the pH 5 to 9 range, then testing should be conducted in buffered aqueous solution at two or three pH values spread throughout the pH 5 to 9 range (**7-9**).

8.9 All analytical standards and stock solutions should be kept in the dark whenever possible. Their stability should be checked frequently by comparison to freshly prepared solutions.

8.10 Only well-validated analytical methods should be used. The precision and accuracy of the photolysis tests will be no better than the precision and accuracy of the method used to determine the concentrations of the parent material.

8.11 If loss of the parent material is observed in control (dark) solutions, additional experiments outside the scope of this test method may be required. Hydrolysis, volatilization, and adsorption are examples of processes that may effect the control solutions.

9. Procedure

9.1 This test method does not attempt to provide stepwise instructions, but does provide guidelines. A certain amount of flexibility must remain so the capability and needs of each investigator can be met.

9.2 *Tier I, Determination of the Test Material's Susceptibility to Undergo Photolysis*:

9.2.1 Expose aqueous solutions of the test material and reference material(s) to a light source for a period up to 5 days in sealed reaction vessels. For sunlight, exposure during the months of April through September is recommended to reduce the variation in the photolysis rate.

9.2.2 Use an initial concentration that is less than the water solubility (one-half the water solubility is recommended) or at environmentally relevant concentrations (1 mg/L), whichever is lower. If the water solubility is too low for handling and analysis, employ 1 % (or less) by volume of acetonitrile as a co-solvent.

9.2.3 Analyze duplicate test solutions at graduated intervals, such as at time zero, 6 h, 2 days, and 5 days. Tests may be terminated after 5 days or when one half-life is exceeded, whichever is shorter.

9.2.4 Analyze one control sample (maintained in the dark) at each of the above sampling times to determine if the compound is chemically stable (hydrolysis or oxidation).

9.3 *Tier II, Determination of Photolysis Rate and Rate Constant*—These parameters may be obtained either by exposure to sunlight or by laboratory measurements.

9.3.1 *Sunlight Exposure*:

9.3.1.1 Using the preliminary rate data obtained in Tier I as a guide, expose dilute aqueous solutions of the test material to sunlight until twice the half-life has been reached.

9.3.1.2 Determine the concentration of the parent material for at least six points from 20 % to 80 % photolysis. Duplicate solutions and duplicate controls should be analyzed at each point.

9.3.1.3 Test the material in reagent water.

9.3.1.4 For materials that photolyze rapidly, start the test at 12:00 noon to get reproducible data.

9.3.1.5 Expose a reference material simultaneously with the test material to serve as an approximate measure of sunlight intensity.

9.3.1.6 If a more realistic estimate of the environmental aqueous photolysis rate is needed, sunlight exposures may be repeated under different atmospheric conditions. After performing the calculations for each exposure (10.1), an average rate constant and half-life can be computed.

9.3.2 *Laboratory Measurements of Photolysis Rates*:

9.3.2.1 Measure the UV-visible absorption spectrum of a dilute aqueous solution of the pure material using a scanning spectrophotometer. Overestimates of molar absorptivities may occur when technical grade substances are tested because the impurities frequently absorb in the same spectral region as the pure chemical. Use the solvent (water or water plus acetonitrile) in the reference cell of the spectrophotometer.

9.3.2.2 Use a stable light source (mercury or xenon arc, fluorescent lamp) and filters to expose a dilute aqueous solution of the material to monochromatic light above 290 nm that the material will absorb.

9.3.2.3 Measure the light intensity with a chemical actinometer. Ideally, the light intensity should be measured continuously during the exposure period. The use of the merry-go-round (**17**) or similar device allows the test material and actinometer to be exposed simultaneously.

9.3.2.4 Recommended actinometers include potassium ferrioxalate (**23**), the benzophenone-sensitized isomerization of 1,3-pentadiene (**32**), malachite green leucocyanide (**33**), o-nitro-benzaldehyde (**34**), Cr (urea)$_6$Cl$_3$ (**35**), ρ-Nitroanisole-pyridine actinometer (**36, 37**) and ρ-Nitroacetophenone-pyridine actinometer (**36, 37**).

9.3.2.5 Determine the concentration of the parent material for at least six points from 20 % to 80 % photolysis. Duplicate solutions and duplicate controls should be analyzed at each point.

9.4 *Tier III, Determination of Phototransformation Products*—Test conditions used in Tier II should provide a satisfactory basis for designing Tier III tests. Some modifications may be required. It may be necessary to use higher concentrations of test material, and radiolabeling may be required to isolate and identify photoproducts. Use of excessively high concentrations should be avoided to minimize the possibility of bimolecular reactions. A material balance inventory should be made to assess what percentage of the products have been identified. The exact design of the tests will depend on the test material. Test procedures in Tier II should provide a framework for these tests.

10. Calculation

10.1 *Calculation Related to Sunlight Exposure* (9.3.1):

10.1.1 Since photolysis reactions are assumed to be first order, a plot of natural log concentration versus time should produce a straight line. Plot ln[P] versus t, where [P] is the concentration of the parent material and perform a linear regression analysis and compute the linear correlation coefficient. In performing the linear regression, each value of ln[P] should be weighted in proportion to the inverse square of its uncertainty. The calculation will be obtained as follows:

$$\ln[P] = -Kt + b \tag{1}$$

where:
K = the first-order rate constant, and
b = natural log of the concentration of the parent material at time zero.

10.1.2 The photolysis half-life ($t_{½}$) can be computed using the equation:

$$t_{½} = (0.693/K) \tag{2}$$

10.1.3 This test method assumes first-order kinetics. The experimental conditions are chosen to simulate environmental conditions and minimize higher order reactions. Deviations from first-order kinetics should be reported, but it is beyond the scope of this test method to provide a detailed treatment.

10.2 *Calculations Related to Monochromatic Laboratory Measurements* (9.3.2):

10.2.1 Calculate the molar absorptivity for the parent material (ϵ) at the wavelength used for photolysis as follows:

$$A = \epsilon lc \text{ or } \epsilon = (A/lc) \tag{3}$$

where:
A = absorbance,
l = pathlength of spectrophotometer cell, cm, and
c = concentration of the material, mol/L.

10.2.2 Quantum yields can be calculated using a multi-step procedure. Plot ln[P] versus t as described in 10.1.1 and obtain a calculation in the form of Eq 1. For weakly absorbing (dilute) solutions (absorbance <0.02), the quantum yield can be calculated as follows (**38**):

$$\Phi_r = (K)/(2.303\ \epsilon_\lambda\ I_\lambda l) \tag{4}$$

where:
Φ_r = reaction quantum yield,
K = laboratory photolysis rate constant from Eq 1,
ϵ_λ = molar absorptivity of the material at a specific wavelength, λ,
I_λ = light intensity passing through the reaction vessel in einsteins per litre second (1 einstein = 1 mol of photons), and
l = cell path length, cm.

I_λ may be determined with an actinometer that completely absorbs all incident light. I_λ is then equal to the photoreaction rate of the actinometer (in moles per litre per second) divided by its reaction quantum yield at wavelength λ. Care should be taken to use the identical conditions used to expose the test material. For an accurate quantum yield calculation, it is critical that the measured light intensity be equal to the intensity passing through the test solution. If an apparatus such as the merry-go-round reactor is used, the actinometer and test material can be exposed simultaneously.

10.2.3 If a reaction vessel with a square or rectangular cross section is used, the pathlength can be measured with a rule. If the vessel has a circular cross section or an irregular shape, the effective or average pathlength should be measured. This determination needs to be performed only once for any set of apparatus. The method of Zepp is outlined as follows (**39**): The photolysis rate for a system in which a large fraction of the light is absorbed is related to the maximum photolysis rate (achieved when all of the light is absorbed) as follows:

$$[((\text{rate})\text{c})/((\text{rate})\text{max})] = X = 1 - 10^{-\epsilon\lambda\iota c} \tag{5}$$

By measuring the maximum photolysis rate when all of the light is absorbed (at C_{max}) and photolysis rates at lower concentrations (c), a plot of – log (1 – X) versus $\epsilon_\lambda c$ yields a straight line with a slope equal to l. Zepp has used the benzophenone sensitized cis- to trans-isomerization of 1,3-pentadiene for pathlength measurements.

10.2.4 *Specific Rate of Absorption* (κ_α)—The specific rate of absorption for a given set of laboratory conditions ($\kappa_{\lambda\text{L}}$) can be calculated from one of the following equations:

$$\kappa_{\alpha\text{L}} = 2.303\ I_{\lambda\epsilon\lambda}\iota \tag{6}$$

$$(-\text{d}[P])/(\text{d}t) = \kappa_{\alpha\text{L}}\Phi_\text{r}[P] \tag{7}$$

Calculating specific rates of absorption that represent environmental conditions ($\kappa_{\alpha E}$) requires the use of several complex equations. The following equations have been used by Zepp et al (**29**):

$$\kappa_{\alpha\text{E}} = (\Sigma[I_{\text{d}\lambda}\,(1 - 10^{-\alpha\lambda\iota\text{d}}) + I_{\text{s}\lambda}\,(1 - 10^{-\alpha\lambda\ \iota\text{s}})]\epsilon\lambda\alpha\lambda^{-1})/(D) \tag{8}$$

where:
$I_{d\lambda}$ = direct irradiance,
$I_{s\lambda}$ = sky irradiance,
αλ = decadic absorption coefficient of water,
l_d = pathlength of direct irradiance beneath the surface of the water,
l_s = pathlength of sky irradiance beneath the surface of the water,
ϵλ = molar absorptivity for the material, and

D = depth of the water body.

$$\iota_d = (D\mu_r)/(\sqrt{\mu_r^2 - \sin^2 Z}) \qquad (9)$$

$$\iota_s = 1.2\,D \qquad (10)$$

where:

z = solar zenith angle, and
μ_r = refractive index of water.

Detailed derivations for Eq 8-10 and methods for calculating $I_{s\lambda}$ and $I_{d\lambda}$ are presented by Zepp and Cline (**26**). They also present a computerized model (available upon request) which incorporates Eq 8-10 and calculates rates of direct photolysis. The model takes into consideration the effects of solar spectral irradiance at the water surface, radiative transfer from air to water, and transmission of sunlight in the water body. A detailed discussion of this approach for calculating direct rates of photolysis is not essential in this test method. This brief description serves only to point out the logic of using such an approach. For more information, Refs **26**, **29**, and **38** are recommended.

10.2.5 *First-Order Rate Constant* (*K*)—The environmental rate constant can be calculated as follows:

$$K = \phi_r \kappa_{\alpha E} \qquad (11)$$

10.2.6 *Half-Life* ($t_{½}$)—See 10.1.2 and 10.1.3.

10.2.7 The calculations in 10.2.5 and 10.2.6 assume that ϕ_r is not a function of wavelength. This is usually true for complex molecules in solution (**40**). The assumption may be tested by repealing 9.3.2 using different exposure wavelengths. Materials for which ϕ_r is a strong function of wavelength are beyond the scope of this test method.

11. Report

11.1 Report all data and details from the Experimental Considerations section.

11.2 *Results*:

11.2.1 *Tier I*—Percent lost of the parent material in the exposed and control samples and the length of the exposure.

11.2.2 *Tier II*—Calculated half-life in either sunlight hours or calendar days, rate constant, and percent loss of the parent material in the controls. Include the linear correlation coefficient from the plot of log concentration versus time as a measure of first-order reaction kinetics. If photolysis was performed in the laboratory, report the UV-visible absorption spectrum and the calculated ϕ_r and $\kappa_{\alpha E}$.

11.2.3 *Tier III*—All products identified, their percent yield, and any information obtained about the reaction mechanism.

11.3 *Experimental Conditions*:

11.3.1 For all experiments report the initial concentration of the test material and any co-solvents used, and a description of the analytical procedures.

11.3.2 *Sunlight Exposure*—Exposure dates and times and total hours of sunlight, the location of the exposure (including latitude and longitude), atmospheric conditions, a description of the apparatus, and results obtained for reference materials.

11.3.3 *Laboratory Exposure*—Complete description of the light source and filters, photolysis apparatus, and the type of actinometer and the results obtained with it.

12. Precision and Bias

12.1 As a test of the Tier I guides, a single operator from each of several laboratories exposed aqueous solutions of 3,4-dichloroaniline and dibenzothiophene to sunlight. Significant losses were observed from the exposed solutions when compared to the controls, indicating the occurrence of phototransformation.

12.2 Even though Tier I is not meant to provide quantitative rate data, the results of the interlaboratory test are included as a guide to the type of data that may be expected from Tier I. The average percent loss of the test material at the end of the indicated exposure period and the precision, calculated as percent relative standard deviation (RSD), are listed in Table 2.

12.3 Results of the Tier I guides using polychromatic laboratory light sources indicated that both of the above materials were susceptible to phototransformation, achieving the goal of Tier I. However, the types of equipment used by the different laboratories were too diverse to make a meaningful quantitative comparison.

TABLE 2 Precision for Sunlight Exposure

Test Material	Water Type	Number of Participants	Exposure Time, h	Exposed Solutions		Control Solutions	
				Avg % Loss	% RSD	Avg % Loss	% RSD
3,4-Dichloroaniline	reagent	4	6	85	16	6.6	140
3,4-Dichloroaniline	natural	4	6	76	28	7.0	120
Dibenzothiophene	reagent	3	120	50[A]	27	0.25	200
Dibenzothiophene	natural	2	120	47[A]	58	4.0	140

[A] Data from one laboratory excluded because of large (>40 %) losses from control solutions.

REFERENCES

(1) U.S. Environmental Protection Agency,“ Chemical Fate Testing Guidelines, Subpart D—Transformation Processes, Section 796.3700, Photolysis in Aqueous Solution in Sunlight,” *Federal Register*, Vol 50, No. 188, 1985, pp. 39285–39296.

(2) U.S. Environmental Protection Agency, “Unsubstituted Phenylenediamines; Proposed Test Rule,” *Federal Register*, Vol 51, No. 3, 1986, pp. 483–490.

(3) Crosby, D. G., and Wong, A. S., “Photodecomposition of 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) in Water,” *Journal of Agricultural and Food Chemistry*, Vol 21, 1973, p. 1052.

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