



Designation: E896 – 92 (Reapproved 2005)^{ε1}

Standard Test Method for Conducting Aqueous Direct Photolysis Tests¹

This standard is issued under the fixed designation E896; 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.

^{ε1} NOTE—A warning statement was editorially added to 6.1 in November 2007.

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
D1193 Specification for Reagent Water
E131 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.

¹ This test method is under the jurisdiction of ASTM Committee E47 on Biological Effects and Environmental Fate and is the direct responsibility of Subcommittee E47.04 on Environmental Fate and Transport of Biologicals and Chemicals.

Current edition approved Aug. 1, 2005. Published August 2005. Originally approved in 1982. Last previous edition approved in 1997 as E896 – 87(1997). DOI: 10.1520/E0896-92R05E01.

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.

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

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 E131).

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 D1193.

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. **Warning**—Mercury has been designated by EPA and many state agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA’s website – <http://www.epa.gov/mercury/faq.htm> - for additional information. Users should be aware that selling mercury and/or mercury containing products into your state may be prohibited by state law.

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

TABLE 1 Suggested Reference Materials for Use in Determining Photolysis Rates

Compound	Half Life in Sunlight ^A	$\phi_r \lambda$ (nm)	Ref.
1. 3,3'-Dichlorobenzidine	1 to 2 min <6 h ^B	0.43, 254 0.053, 313	39 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. <i>p</i> -Nitroanisole Actinometer			44, 45
6. <i>p</i> -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.

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.

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

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