
40 C.F.R. § 795.70

Indirect photolysis screening test: Sunlight photolysis in waters containing dissolved humic substances.

(a) *Introduction.* (1) Chemicals dissolved in natural waters are subject to two types of photoreaction. In the first case, the chemical of interest absorbs sunlight directly and is transformed to products when unstable excited states of the molecule decompose. In the second case, reaction of dissolved chemical is the result of chemical or electronic excitation transfer from light-absorbing humic species in the natural water. In contrast to direct photolysis, this photoreaction is governed initially by the spectroscopic properties of the natural water.

(2) In general, both indirect and direct processes can proceed simultaneously. Under favorable conditions the measurement of a photoreaction rate constant in sunlight (k_{pE}) in a natural water body will yield a net value that is the sum of two first-order reaction rate constants for the direct (k_{DE}) and indirect (k_{IE}) pathways which can be expressed by the relationship

Equation 1

$$k_{pE} = k_{DE} + k_{IE}.$$

This relationship is obtained when the reaction volume is optically thin so that a negligible fraction of the incident light is absorbed and is sufficiently dilute in test chemical; thus the direct and indirect photoreaction processes become first-order.

(3) In pure water only, direct photoreaction is possible, although hydrolysis, biotransformation, sorption, and volatilization also can decrease the concentration of a test chemical. By measuring k_{pE} in a natural water and k_{DE} in pure water, k_{IE} can be calculated.

(4) Two protocols have been written that measure k_{DE} in sunlight or predict k_{DE} in sunlight from laboratory measurements with monochromatic light (USEPA (1984) under paragraph (f)(14) and (15) of this section; Mill et al. (1981) under paragraph (f)(9) of this section; Mill et al. (1982) under paragraph (f)(10) of this section; Mill et al. (1983) under paragraphs (f)(11) of this section). As a preface to the use of the present protocol, it is not necessary to know k_{DE} ; it will be determined under conditions that definitively establish whether k_{IE} is significant with respect to k_{DE} .

(5) This protocol provides a cost effective test method for measuring k_{IE} for test chemicals in a natural water (synthetic humic water, SHW) derived from commercial humic material. It describes the preparation and standardization of SHW. To implement the method, a test chemical is exposed to sunlight in round tubes containing SHW and tubes containing pure water for defined periods of time based on a screening test.

(6) To correct for variations in solar irradiance during the reaction period, an actinometer is simultaneously

insolated. From these data, an indirect photoreaction rate constant is calculated that is applicable to clear-sky, near-surface, conditions in fresh water bodies.

(7) In contrast to k_{DE} , which, once measured, can be calculated for different seasons and latitudes, k_{IE} only applies to the season and latitude for which it is determined. This condition exists because the solar action spectrum for indirect photoreaction in humic-containing waters is not generally known and would be expected to change for different test chemicals. For this reason, k_{pE} , which contains k_{IE} , is likewise valid only for the experimental data and latitude.

(8) The value of k_{pE} represents an atypical quantity because k_{IE} will change somewhat from water body to water body as the amount and quality of dissolved aquatic humic substances change. Studies have shown, however, that for optically-matched natural waters, these differences are usually within a factor of two (Zepp et al. (1981) under paragraph (f)(17) of this section).

(9) This protocol consists of three separate phases that should be completed in the following order: In Phase 1, SHW is prepared and adjusted; in Phase 2, the test chemical is irradiated in SHW and pure water (PW) to obtain approximate sunlight photoreaction rate constants and to determine whether direct and indirect photoprocesses are important; in Phase 3, the test chemical is again irradiated in PW and SHW. To correct for photobleaching of SHW and also solar irradiance variations, tubes containing SHW and actinometer solutions are exposed simultaneously. From these data k_{pE} is calculated that is the sum of k_{IE} and k_{DE} (Equation 1) (Winterle and Mill (1985) under paragraph (f)(12) of this section).

(b) *Phase 1—Preparation and standardization of synthetic natural water—(1) Approach.* (i) Recent studies have demonstrated that natural waters can promote the indirect (or sensitized) photoreaction of dissolved organic chemicals. This reactivity is imparted by dissolved organic material (DOM) in the form of humic substances. These materials absorb sunlight and produce reactive intermediates that include singlet oxygen (1O_2) (Zepp et al. (1977) under paragraph (f)(20) of this section, Zepp et al. (1981) under paragraph (f)(17) of this section, Zepp et al. (1981) under paragraph (f)(18) of this section, Wolff et al. (1981) under paragraph (f)(16) of this section, Haag et al. (1984) under paragraph (f)(6) of this section, Haag et al. (1984) under paragraph (f)(7) of this section); peroxy radicals (RO_2^-) (Mill et al. (1981) under paragraph (f)(9) of this section; Mill et al. (1983) under paragraph (f)(8) of this section); hydroxyl radicals (HO^-) (Mill et al. (1981) under paragraph (f)(9) of this section, Draper and Crosby (1981, 1984) under paragraphs (f)(3) and (4) of this section); superoxide anion (O_2^{--}) and hydroperoxy radicals (HO^-). (Cooper and Zika (1983) under paragraph (f)(1) of this section, Draper and Crosby (1983) under paragraph (f)(2) of this section); and triplet excited states of the humic substances (Zepp et al. (1981) under paragraph (f)(17) of this section, Zepp et al. (1985) under paragraph (f)(21) of this section). Synthetic humic waters, prepared by extracting commercial humic or fulvic materials with water, photoreact similarly to natural waters when optically matched (Zepp et al. (1981) under paragraphs (f)(17) and (18) of this section).

(ii) The indirect photoreactivity of a chemical in a natural water will depend on its response to these reactive intermediates, and possibly others yet unknown, as well as the ability of the water to generate such species. This latter feature will vary from water-to-water in an unpredictable way, judged by the complexity of the situation.

(iii) The approach to standardizing a test for indirect photoreactivity is to use a synthetic humic water (SHW) prepared by water-extracting commercial humic material. This material is inexpensive, and available to any laboratory, in contrast to a specific natural water. The SHW can be diluted to a dissolved organic carbon (DOC) content and uv-visible absorbance typical of most surface fresh waters.

(iv) In recent studies it has been found that the reactivity of SHW mixtures depends on pH, and also the history of sunlight exposure (Mill et al. (1983) under paragraph (f)(11) of this section). The SHW solutions initially photobleach with a time-dependent rate constant. As such, an SHW test system has been designed that is buffered to maintain pH and is pre-aged in sunlight to produce, subsequently, a predictable bleaching behavior.

(v) The purpose of Phase 1 is to prepare, pre-age, and dilute SHW to a standard mixture under defined, reproducible conditions.

(2) *Procedure.* (i) Twenty grams of Aldrich humic acid are added to a clean 2-liter Pyrex Erlenmeyer flask. The flask is filled with 2 liters of 0.1 percent NaOH solution. A stir bar is added to the flask, the flask is capped, and the solution is stirred for 1 hour at room temperature. At the end of this time the dark brown supernatant is decanted off and either filtered through coarse filter paper or centrifuged and then filtered through 0.4µm microfilter. The pH is adjusted to 7.0 with dilute H₂SO₄ and filter sterilized through a 0.2µm filter into a rigorously cleaned 2-liter Erlenmeyer flask. This mixture contains roughly 60 ppm DOC and the absorbance (in a 1 cm path length cell) is approximately 1.7 at 313 nm and 0.7 at 370 nm.

(ii) Pre-aging is accomplished by exposing the concentrated solution in the 2-liter flask to direct sunlight for 4 days in early spring or late fall; 3 days in late spring, summer, or early fall. At this time the absorbance of the solution is measured at 370 nm, and a dilution factor is calculated to decrease the absorbance to 0.50 in a 1 cm path length cell. If necessary, the pH is re-adjusted to 7.0. Finally, the mixture is brought to exact dilution with a precalculated volume of reagent-grade water to give a final absorbance of 0.500 in a 1-cm path length cell at 370 nm. It is tightly capped and refrigerated.

(iii) This mixture is SHW stock solution. Before use it is diluted 10-fold with 0.010 M phosphate buffer to produce a pH 7.0 mixture with an absorbance of 5.00×10^{-2} at 370 nm, and a dissolved organic carbon of about 5 ppm. Such values are characteristic of many surface fresh waters.

(3) *Rationale.* The foregoing procedure is designed to produce a standard humic-containing solution that is pH controlled, and sufficiently aged that its photobleaching first-order rate constant is not time dependent. It has been demonstrated that after 7 days of winter sunlight exposure, SHW solutions photobleached with a nearly constant rate constant (Mill et al. (1983) under paragraph (f)(11) of this section).

This document is only available to subscribers. Please log in or purchase access.

[Purchase Login](#)