

A CONVENIENT TEST METHOD FOR PHOTOCHEMICAL TRANSFORMATION OF POLLUTANTS
IN THE AQUATIC ENVIRONMENT.

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Abstract

A test method, based on a modified Xenotest 1200, is described, and has been proved to be convenient for determination of the rate of photolytical degradation and by that it can make a valuable contribution to the evaluation of environmental stability of organic compounds. The test method was applied to testing of photochemical degradation of organic chemicals in aquatic media. Solutions of six chlorinated phenolic substances, 8-quinolinol and 9,10-anthraquinone were illuminated with filtered light, simulating daylight at controlled conditions. Quantum yields of photochemical degradation and half lifetimes (of conversion) were calculated using a sun spectrum at 60° N. Chlorophenols absorbing light at 295 - 350 nm were converted and theoretical half lifetimes of 0.75 -2.6 hours were obtained. The photochemical conversion of 8-quinolinol was slow. Anthraquinone was studied in ethanol/water and the degradation corresponded to a half lifetime of 2.8 hours.

Introduction

The evaluation of the stability of organic compounds in the aquatic environment has with few exceptions taken only the biodegradability into consideration. The lifetime of an organic compound in the environment depends, however, also on physical and chemical processes, that alter the chemical structure of the compound.

In the assessment of the environmental lifetime of organic compounds and thereby the risk, also abiotic processes therefore have to be considered, and to determine the quantitative contribution of these processes, suitable test methods are required.

In the air compartment biological processes are of minor interest compared to physical and chemical processes like photodegradation and chemical redox reactions. In soil and in water, especially in the interface between water and sediment, the biological processes, like aerobic and anaerobic degradation, are predominant in converting the chemical structure. However, in the water compartment hydrolysis and photochemical transformation may play an important part in the fate of an organic compound. The photochemical transformation reactions are especially important in the upper layers of the water body (1-4).

Photochemical degradation irreversibly changes the chemical structure of an organic compound. In primary photolysis the molecule by itself is excited by incident light energy. Photolysis of a molecule can also be dependent on another excited molecule, *i.e.* sensitization. Photolysis can result in a cleavage of chemical bonds, dimerisation, oxidation, hydrolysis or rearrangement (2,4).

Studies of the kinetics of photochemical transformation of organic compounds in water from the environmental point of view require a light source with either constant intensity or the possibility to quantify the variation in intensity. Recently methods using the polychromatic xenon light spectrum simulating sunlight was proposed (3,5).

By this methodology it is possible to make an estimate of the environmental aquatic lifetime of an organic compound subjected to direct photochemical transformation. The theoretical lifetime is derived from the experimentally determined quantum yield of conversion, *i.e.* the number of photochemically transformed molecules per number of photons absorbed (5). The lifetime of a chemical compound subjected to direct phototransformation in the aquatic compartment depends not only on the quantum yield of conversion and the absorption spectrum of the compound but also on the light intensity, spectral distribution of daylight and a variety of system-related parameters such as latitude, season, the ozone layer thickness, the cloud cover, the light attenuation in the water, the concentration of suspended solids, *etc.*

Criteria on methods for determination of photochemical conversion has been published together with an evaluation of three earlier proposed procedures (5).

The present report describes a photochemical transformation study of a series of compounds where the illumination has been performed in a modified Xenotest 1200 apparatus. The apparatus was applied to illumination of up to 40 simultaneous samples of aquatic solutions of organic chemicals.

The experimental performance and calculations of quantum yields of conversion and theoretical half lifetimes were essentially according to an earlier procedure (5) and are reported with details elsewhere (6).

Materials and methods

The tested chlorophenols were purchased from Aldrich-Chemie, FRG (2,4-dichlorophenol, purity 97%, 2,3,4-trichlorophenol, purity not declared, 2,3,4,5-tetrachlorophenol, purity 98%, and pentachlorophenol, purity 97%). 2,4,6-Trichlorophenol was obtained from Schuchardt, Munich, FRG. 4,5,6-Trichloroguaiacol was a gift from Dr. A. Neilson at this institute. 8-Quinolino (hy-

droxyquinoline) p.a. and 9,10-anthraquinone were obtained from E. Merck AG, Darmstadt, FRG. Solutions of test substances in 25 mM sodium phosphate, pH 7.00, were prepared either by dissolving directly or in a small volume of ethanol prior to dilution. Samples of these solutions were illuminated in a Xenotest 1200 apparatus (Original Hanau, Heraeus GmbH, Hanau, FRG). A principal drawing of the set of lamps and samples is shown in Fig 1. The light source consisted of three vertically oriented 4.5 kW xenon lamps fitted with reflectors for ultraviolet and visible light. Xenon lamps age and a lamp would last about 1500 hours. In the test device, one lamp was replaced every 500 hours and the samples will thus be constantly illuminated by one new, one old and one medium-aged lamp. It was assumed that ageing of the lamps did not affect the spectral distribution of light intensity, only the total emitted light.

Infrared irradiation was absorbed in a circulating water system. Radiation below 295 nm was cut off by a Suprax-filter. Samples of 3 ml volume were illuminated in 1x1x4 cm³ teflon-capped quartz cuvettes. The cuvettes were fixed at a constant distance from the light source and rotated in a circulating cuvette holder with a rotating speed of approximately 1 turn per min. The rotating cuvette holder further warrants the uniform illumination. In the cuvette holder up to 40 cuvettes may be illuminated. At least 10 such holders with a total of ca 400 samples may be placed in the merry-go-round. The ambient air temperature was controlled at 25±0.2°C except in a test of the temperature dependence.

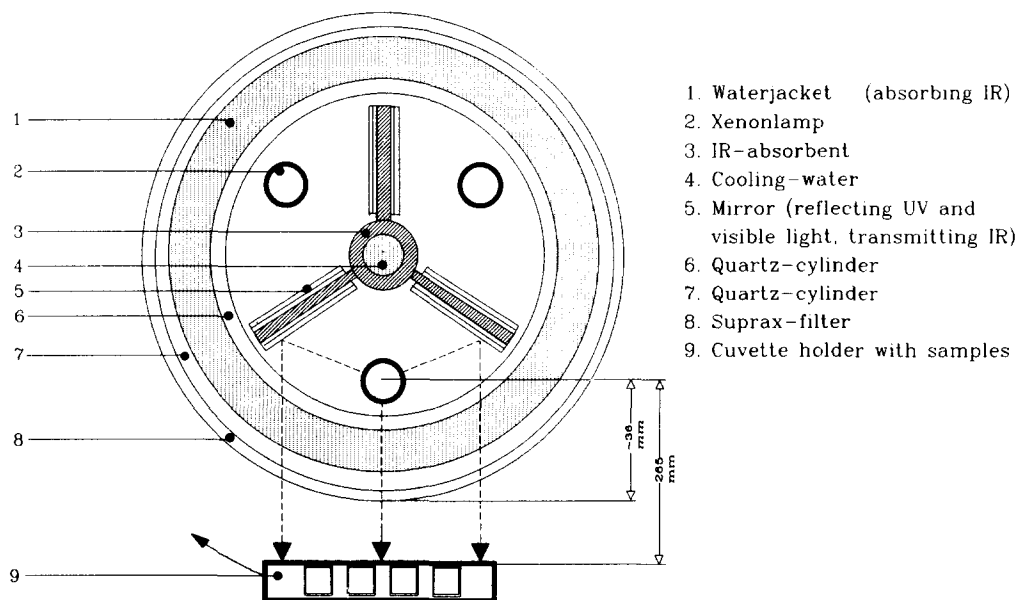


Fig. 1 The Xenotest 1200 apparatus, modified for illumination of samples of organic substances in aqueous solution.

The incident light intensity of the xenon light source was measured using a chemical actinometer with a known quantum yield of conversion (7). The actinometric solution consisted of 10 mM uranyl nitrate, and 50 mM oxalic acid, (p.a., E. Merck AG, Darmstadt, FRG). Actinometric solutions were

illuminated in duplicates for three different periods together with the test solutions. The decrease in oxalic acid concentration was analysed as total organic carbon in an Astro Model 1850, Total Organic Carbon Analyzer (Astro Water Pollution and Control Division, Houston, USA). The method presented here, using the uranyl oxalate actinometer, is limited to tests of substances absorbing below 500 nm.

Chlorophenolic substances were analysed after acetylation by capillary gas chromatography (8). 8-Quinolol was determined fluorimetrically by excitation at 360 nm (9). Emitted light was recorded at 520 nm and compared with solutions of known concentrations of quinolol. Anthraquinone was analysed by gas chromatography according to a published procedure (10). Absorbance spectra were recorded using a Beckman DU 8 spectrophotometer.

Half lifetimes of photochemical conversion of the substances were calculated using a solar spectrum on a horizontal surface representing 60°N at noon June 21st (Stockholm latitude). The spectrum was calculated according to a model (11), using the following variables: Ångströms turbidity coefficients $\alpha = 1.14$, $B = 0.050$; amount of precipitable water 1.8 cm; ozone 0.350 matm x cm; surface reflectance 0.2 and the air-pressure 1000 hPa. Furthermore, a clear cloudless sky and no shadowing effects of surface or shore vegetation was assumed.

Results and discussion

Tests of photochemical conversion of a series of model compounds were performed in a modified Xenotest 1200 apparatus. Artificial polychromatic xenon light was used instead of daylight because of the variation of the latter with season and weather conditions. Fitted with a suitable filter the spectral distribution of light intensity simulated the sunlight spectrum at the surface of the earth (Fig. 2a and b).

The intensity of the incident light in the 295 - 500 nm interval was measured using a uranyl oxalate actinometer (Fig. 2c). All tested substances absorbed ultraviolet and visible light within this interval of the sunlight spectrum. The measurements of the incident light in two test series gave 1.43 and 1.46×10^{16} photons/s and cm^2 , respectively.

Absorption of light by the tested substances was followed by conversion as shown by analysis of the remaining parent compounds (Fig. 3 and Table 1). The amount of compound converted during the illumination period was calculated and expressed in molecules /s x cm^2 (Table 1). The illumination period was chosen to give 10-25 % conversion of the original concentration, in order to avoid secondary processes and to minimize the correction for absorption changes in the samples. The absorption spectra were recorded before and after the illumination period and those of 4,5,6-trichloroguaiacol are shown in Fig. 2d and e.

The dependence of start concentration was studied in a separate experiment using cuvettes of different pathlength. 2,4-Dichlorophenol was illuminated in 2, 5 and 10 mm cuvettes with the same widths and heights in duplicates. The concentrations were 0.967, 0.484, and 0.193 mM and the volumes were adjusted to give the same area exposed to the light source (3 cm^2). After illumination and analysis of remaining parent compound the relative rate of conversion was calculated after approximately 20% photolytic conversion of the parent compound. No effects of

secondary processes on the primary photolytic conversion were indicated at this stage of the photolysis. No significant effects on the rate of conversion were observed upon variation of the ambient temperature between 17 and 34 °C.

The spectral distribution of the incident xenon light at the vertical surface of the sample cuvettes was calculated using a xenon lamp intensity spectrum and a value of the integrated light intensity measured by the uranyl oxalate actinometer. The lamp spectrum, shown in Fig. 2a, was kindly provided by the National Testing Institute.

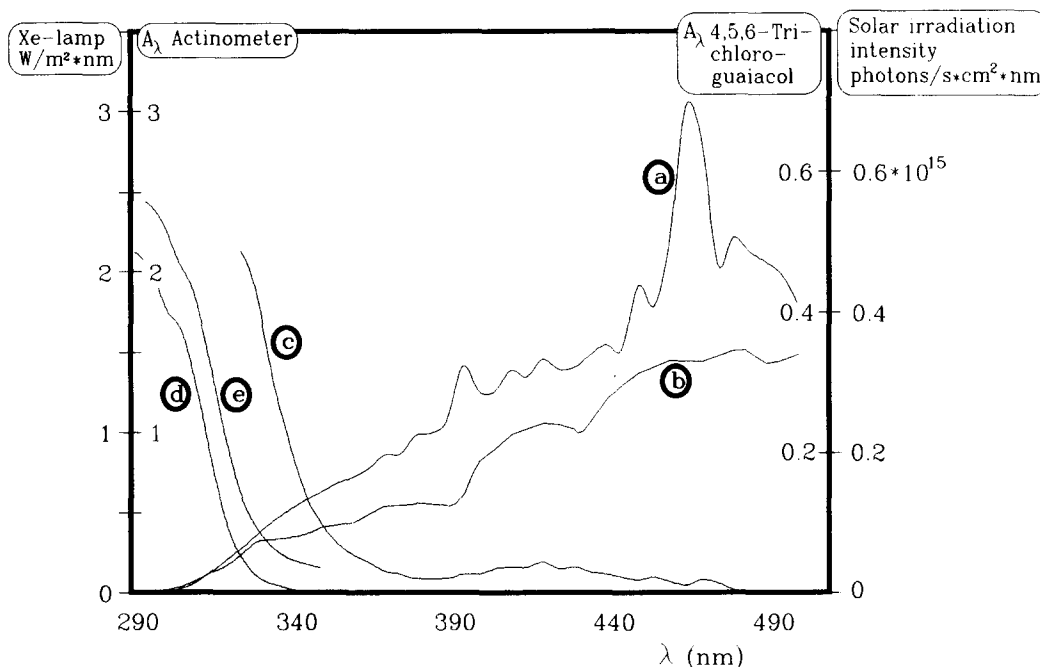


Fig. 2 Ultraviolet-visible spectra of filtered light of the Xenotest 1200 apparatus (a), yearly maximum of daylight at 60° N (b), the absorption spectrum of 10 mM uranyl nitrate (actinometer) (c), and spectra of 0.151 mM 4,5,6-trichloroguaiacol, before (d) and after (e) 15 min of illumination in the Xenotest 1200 apparatus.

Quantum yields of conversion were then calculated from the number of converted molecules and the number of absorbed photons, where the latter represents the sum of absorbed light intensity corrected for absorption changes due to conversion during the illumination period. The results of the test sample series are presented in Table 1. Obtained values of quantum yields corresponded well with earlier published values of 2,4-dichlorophenol at pH 7.0, and pentachlorophenol (5). In the series of chlorinated phenolic substances, the quantum yields seemed to decrease with increasing number of chlorines in the molecule.

Half lifetimes of substances exposed to sunlight were then calculated from the molar absorptivity, quantum yields and a sunlight spectrum. Molar absorptivity and quantum yields were measured and calculated as described above. A sunlight spectrum, representing the Stockholm latitude, 60° N, at noon on June 21st 1987, *i. e.* the maximum of the year, was calculated using

a model (11). Corrections were made for the actual values of humidity and concentrations of ozone and aerosols. Furthermore, a cloudless sky was assumed. The sunlight spectrum is shown in Fig. 2a. Thus, so called theoretical half lifetimes were calculated and the obtained results are presented in Table 1. These results show that the tested chlorinated phenolic substances will be converted photochemically at a rate with half lifetimes of 0.75 - 2.6 hours, when dissolved in the top millimeters of a waterbody in the Stockholm area, and at the year-maximum of light intensity.

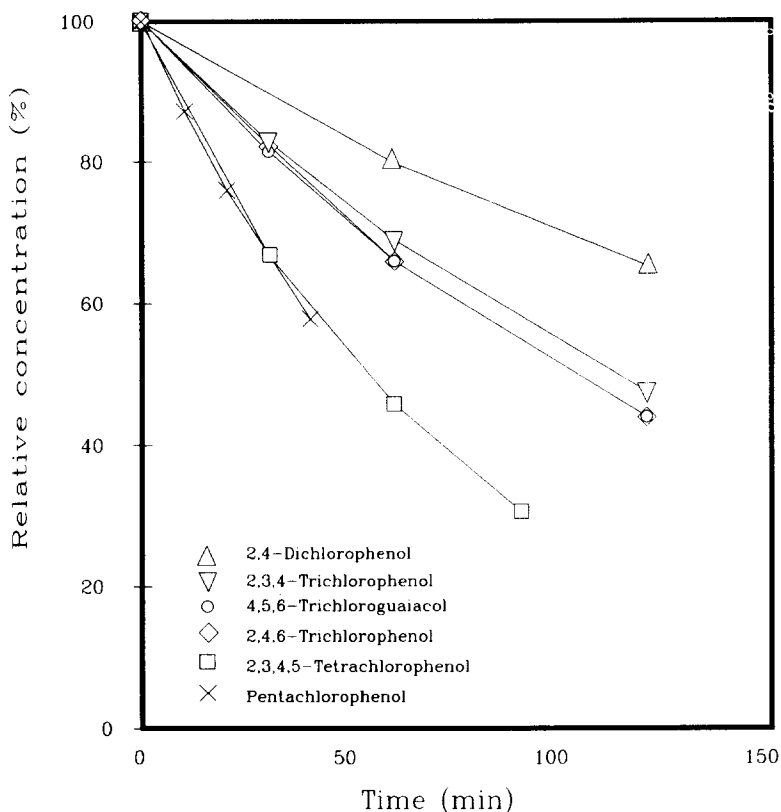


Fig. 3 Decrease in concentrations of chlorinated phenolic substances upon illumination in Xenotest 1200 apparatus.

The quinolinol was photolyzed at a much lower rate. Half lifetimes of 64 and 40 hours were obtained in two tests of which the former was somewhat less accurate, due to shorter illumination times and unsuitably high concentrations. Anthraquinone, on the other hand, was photolyzed with a half lifetime of 2.8 hours, but this substance was tested in an ethanol/water mixture.

We used a calculated yearly maximum of sunlight intensity at 60°N (Stockholm latitude) for the calculations of half lifetimes of the investigated substances. This intensity was 20-30% higher than the year average intensity at 40°N that was used earlier (12,13). The calculated half lifetimes would therefore agree within the same order of magnitude. Using earlier published

Table 1. Test of photochemical transformation in Xenotest 1200.

Tested compound	Start concentration (μM)	Rate of conversion (molecules /s x cm^3) x10 ⁻¹²	Rate of absorption (photons /s x cm^3) x10 ⁻¹⁴	Quantum yield of conversion	Half lifetime (hr)
2,4-Dichloropheno1	967	34,1	3,68	0,0926	2,5
"-	967	30,4	2,91	0,104	2,6
2,3,4-Trichloropheno1	267	15,1	4,15	0,0363	1,7
2,4,6-Trichloropheno1	180	11,2	6,17	0,0190	1,2
4,5,6-Trichloroguaiacol	132	7,73	2,35	0,0328	1,6
"-	151	9,36	3,07	0,0305	1,6
2,3,4,5-Tetrachloropheno1	79,2	8,63	3,94	0,0219	0,88
Pentachloropheno1	21,6	3,21	2,50	0,0129	0,75
"-	21,6	2,81	2,89	0,00972	0,96
8-Quinolino1	993	1,51	89,0	0,000170	64
"-	333	1,17	52,3	0,000224	40
9,10-Anthraquinone*	115	4,35	12,5	0,0035	2,8

*The medium contained 99% ethanol and 1% 25 mM sodium phosphate, pH 7.00.

values on pentachlorophenol, the calculated half lifetime of 0.97 hours was very well correlated with 0.75 and 0.96 hours in this study (4). Our absorption data of 2,4-dichlorophenol at pH 7, the solar spectrum of Zepp and Cline, and earlier published quantum yields gave half lifetimes of 1.6 and 2.3 hours, fairly well in accordance with 2.5 and 2.6 hours in our tests (5,12). The described test method, based on the modified Xenotest 1200, fulfills the criteria specified in the evaluation of a ringtest of photodegradation methods (5). The test method has been proved to be convenient for determination of the rate of photolytical degradation and by that it can make a valuable contribution to the evaluation of environmental stability of organic compounds.

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