

Technical Report

No 3

**An Assessment of Test Methods for
Photodegradation of Chemicals in the
Environment**

August 1991

ISSN-0773-8072-3

ECETOC

3 Aug. 1981

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A. SUMMARY

This report has been produced by an ECETOC Task Force and is intended to contribute to the development and selection of test methods for determining the photodegradation of chemicals in the environment. It is particularly relevant to the requirements of laws and regulations in which there may be a need for photodegradation data, for example in the European Communities' 6th Amendment to the 1967 Directive on the Classification, Labelling and Packaging of Dangerous Substances. In this Amendment, abiotic degradation tests are foreseen in the "base-set" screening tests for new chemicals produced at above 1 tonne per year, and tests at "level 2" may be required for new chemicals whose production exceeds 1000 tonnes per year. Photodegradation is one example of an abiotic route of degradation. Test methods for photodegradation in air, water and soil have been considered by an expert group in the OECD's Chemicals Testing Programme with the aim of producing internationally-acceptable guidelines useful for legislative purposes.

Photodegradation includes not only the process taking place when a material is degraded because it has itself absorbed light, but also degradation by reaction with the products of a photo-chemical reaction, for example as occurs naturally when hydroxyl radical is produced photochemically and oxidizes a material in the air. Photodegradation may take place in the atmosphere, in water, or in the solid state (soil). Degradation in the solid state includes reaction of the substance in or on another solid. In the present report, general criteria which experimental methods must meet in order to be relevant to photodegradation in the environment are considered. Existing and proposed test methods are then reviewed in the light of these criteria. On the basis of the reviews, and a consideration of other theoretical and practical requirements, guidelines for relevant test methods are defined and the design of experiments in air, in water and in the presence of the solid phase are discussed. Further work which is considered necessary in order to improve the methodology for assessing the photodegradability of chemicals in the environment is recommended.

Criteria for Relevant Test Methodologies

The criteria which define a valid and relevant test method may be divided into those which apply generally and those which are specific to a test in air and water, or on a solid.

The general criteria include :

- a) A knowledge of the compartment (air, water, soil) of the environment in which the substance will occur. This enables the appropriate test medium or media to be chosen.
- b) An awareness of whether the compound under study will degrade by a primary photochemical mechanism in which it absorbs light itself, or by a secondary route involving naturally-occurring photochemically-generated reactive species eg. hydroxyl radical, ozone or singlet oxygen.
- c) Careful selection and design of the light source if natural daylight is not reliably available, with limitation of the spectrum to wavelengths found in natural light, and satisfactory measurement of the light intensity. The characteristics of the artificial light source should be described.
- d) Use and/or, if necessary, development of adequate analytical methods for the test substance.

Special criteria applying to tests in air include :

- a) Consideration of the reaction of the material with photochemically-generated species (in order of importance, hydroxyl radical and ozone) in separate studies each designed to simulate the corresponding natural processes. The study of the primary photochemical degradation of the chemical is only of secondary importance.
- b) Adequate allowance for dark reactions and wall reactions.
- c) Allowance for the possibility that the material may react in the form of a homogeneous aerosol or adsorbed/absorbed on/in other aerosols, as well as reacting as a vapour.

Additional special criteria applying to a test in water include :

- a) Proof that the kinetics are concentration-independent, and the

selection of a test-material concentration such that the test simulates the conditions occurring in the environment as closely as is practically possible.

b) The use of co-solvents for solubilization purposes.

Special criteria for test on a solid surface :

It is important to use a solid whose properties are relevant to environmental processes.

Assessment of Existing Test Methodologies

In Air. With regard to test methods in air, the Fujiki, GSF, Hendry, Klöpffer and ASTM tests (or proposed tests) are considered.

- The Fujiki test (as proposed to OECD) involves primary photochemical degradation only, and also suffers from some shortcomings in technique. It is not regarded as a relevant test.
- The GSF test (as proposed to OECD) consists of irradiation of the test substance on silica gel. It is thus difficult to relate the results to actual reactions occurring in air, and there are insufficient data available to establish such a relationship. Furthermore, the inherent reactivity of silica gel with chemicals is a major confounding factor in interpreting the test results.
- The Hendry method, a two-step procedure, does include both direct photochemical breakdown and secondary reactions with photochemically-generated species. Its first step is a purely theoretical calculation of a photodegradation rate, which, however has only a predictive value because of the general lack of sufficient data on which to base the calculations. The second step approaches most closely an acceptable method. It involves separate experimental determinations of the rates of primary photochemical degradation and of degradation by reactions with hydroxyl radical and ozone.
- The ASTM method is related to the Hendry proposal, but also adds a third step : characterisation of the products of degradation.

- The Klöpffer test simulates gas-phase hydroxyl reactions in solution, but at present there are no fundamental research results which allow a correlation of the findings with reactions in air.

In Water. The existing test methods for degradation in water include those by EPA, and the proposals by ASTM and Battelle.

- The EPA method, (as proposed to OECD) although probably satisfactory for materials absorbing mainly at longer wavelengths, suffers from experimental difficulties at shorter wavelengths (below 330 nm). These arise from the transmission properties of the glasses used, the response of the actinometers, and the spectral interference of impurities in the test material. There are also problems in reconciling the requirements of low optical density and the availability of sufficient material for analysis. The recommendation that sunlight should be used is a further source of difficulty.
- A draft (but not approved) ASTM proposal and a Battelle proposal approach more closely an acceptable method, but still involve problems, discussed in more detail in the body of the present report.

In Soil. Observation of the normal fate of "industrial" organic chemicals has shown that it is unlikely that they will contaminate the soil in relevant concentrations except by accident. Some references to methods for the study of the photodegradation of pesticides are given.

Conclusions

1. Photodegradation is likely to be the predominating process for the elimination of chemicals in the atmosphere where biodegradation is normally unlikely. In order of importance, OH• radical, O₃, and direct photolysis should be investigated. None of the test methods formerly proposed to OECD are relevant to photodegradation in the air and it is rather improbable that they can be made suitable in the future without great modification. For chemicals of low tonnage production for which a

proof can be given that significant accumulation in the environment is unlikely, there is no need for a photodegradation test. This means that in general no screening test is necessary at MPD (OECD) or Base Set (6th Amendment-EEC) level. For chemicals produced in larger tonnage and for those cases where significant accumulation in the environment may occur, the development of adequate, and inevitably more sophisticated, test methods is in principle justified. In the development of such a method it is essential to consider the criteria and safeguards detailed in the present report.

2. In water, biodegradation will always be the most likely pathway for the elimination of chemicals. Nevertheless photodegradation is a potential degradation pathway of many chemicals in water, in particular when biodegradation or other chemical process are too slow to be effective. Because photochemical reactions occur predominantly at the water surface, an assessment of aquatic photodegradation is relevant only when the concentration of the chemical is significant in relation to measured toxic or ecotoxic effects. As outlined in the report, some of the currently-proposed methods can be used as a reliable basis for the development of a relevant test methodology.
3. It is emphasised that on soil, photodegradation of industrial chemicals is the least likely way of elimination and should only be considered in exceptional cases.

Future Development of Test Procedures

Air : an adequate procedure could be based on

- i) theoretical calculation of the reaction rate of the chemical with $\text{OH}\cdot$ radicals (believed to be the major contributor to photodegradation in air) to give an approximate idea of lifetime. This serves only as a guide to the experimental phase.
- ii) experimental determination of the reaction rate of the chemical with $\text{OH}\cdot$ radicals (Cox, Clyne, Zellner, Pitts methods may be suitable), and with ozone.

Water. The photodegradability of a compound in water should be

carried out in three stages : lifetime determination, identification of the important photoproducts, and secondary photoreaction analysis (of less importance). A detailed methodology for the first of these is proposed and should be developed by ring-testing of a suitable range of chemicals. The second and third stages involve essentially the development of adequate analytical methods and no general methodology can be given.

Soil. With regard to photodegradation on solids, it is not possible at present to ~~recommend~~ any particular method, but suggestions regarding the development of a method are made.

B. INTRODUCTION

Photodegradation is one of the possible routes for the elimination of man-made chemicals from the environment. The process may occur with chemicals in air, soil or water, and the importance of photodegradation will vary widely according to the medium. Photodegradation is likely to be the predominant elimination process in the atmosphere, where biodegradation is normally unlikely. In water and soil, biodegradation will be the most likely pathway for elimination, and hydrolysis is also possible. Especially when biodegradation or other processes in water are too slow to be effective, photodegradation may become the most important degradation route. Since photochemical reactions occur only at the water surface, an assessment of aquatic photodegradation is relevant only when the concentration of the chemical is significant in relation to measured toxic or ecotoxic effects. Trace materials in the water can influence the photochemical reactions. For chemicals which biodegrade only slowly in soil, their removal by photodegradation should be considered, but the conditions in soil seem even less favourable for this process as sunlight is absorbed in the surface layers of the soil.

Both industry and the legislative authorities have an interest in the photodegradation of chemicals that reach the environment and possess the potential of causing adverse effects. Test methods have been proposed and discussed, but it is not clear which, if any, of them are adequate scientifically and give results which

are relevant to the actual behaviour of chemicals in the environment. ECETOC therefore set up a Task Force with terms of reference as follows :

"To review the state of the art in photodegradation, to assess and make a constructive critique of existing test methods; and to define what work needs to be done to improve the methodology for assessing the photodegradation of chemicals in the environment".

Before starting the review of proposed test methods and methodologies, the Task Force laid down the criteria to be met by a test method if it was to be scientifically adequate and relevant to the behaviour of chemicals in the environment. The existing proposals were then assessed in the light of these criteria, which also served as a basis of guidelines for relevant practical methodologies.

During this work the results of more basic studies in a number of non-industry laboratories were taken into account by contacts with a few expert scientists in this field. While the contents of this report are wholly the responsibility of ECETOC, we acknowledge with pleasure helpful discussion with Professors J.N. Pitts Jr. (University of Riverside, California) in the U.S.A.; K.H. Becker (University of Wuppertal) and W. Stoeber (Fraunhofer-Institut, Münster) from West Germany; and Dr. D.A. Cox from Harwell, UK.

C. CRITERIA AND THE ASSESSMENT OF CURRENT METHODOLOGIES.

1. GENERAL CRITERIA

There are certain basic criteria which apply to the assessment of photodegradation irrespective of the medium in which the chemical appears.

1.1. Environmental Compartment and Concentration

Before considering the photodegradation of a chemical, it is obviously necessary to know in which compartment of the environment it occurs, and, in what concentration. If these

are not known from quantitative assay then approximate values must be deduced from the physico-chemical properties, production process, use and disposal pattern of the material.

This knowledge, or these deductions, facilitate a definition of the basic parameters for the experimentation to be relevant, ie. in the appropriate environmental medium and under conditions such that the results can be extrapolated to the expected environmental concentration(s). It should be noted that low concentrations in the atmosphere may correspond to a large amount of material in total, considering the large volume of the atmosphere. For poorly-volatile substances, the dispersion may be enhanced by air movement, aerosol formation in and co-distillation into the environment.

1.2. Primary and Secondary Photodegradation

It is essential to distinguish between primary and secondary photodegradation in considering photo-reactions in the environment.

In primary photo-reactions light interacts with the chemical directly by absorption, or indirectly by energy transfer from an excited photo-sensitiser. In secondary photo-reactions the chemical reacts with photolytically-generated radicals (eg. hydroxyl radical); ozone ; singlet oxygen; or a photochemically-generated base which catalyses hydrolysis , etc. Secondary reactions are of major importance in air, especially for compounds which do not absorb light under tropospheric conditions, ie. cannot undergo a primary photochemical process.

It is very difficult to estimate the exact proportion of the two classes of mechanism involved in environmental photodegradation. Whereas in air, secondary photo-reactions with OH[•] radicals and ozone will be predominant, primary photo-reaction may take place in the stratosphere. It has also been suggested (57) (58) that secondary OH[•] reactions are sometimes

preceded by primary photodegradation in the stratosphere (e.g. of halocarbons). In water it is generally accepted that the primary photodegradation will prevail when the chemical itself absorbs light. On soil, the prevailing mechanism of photodegradation is at present not clearly established.

Thus, in summary, a relevant methodology for photodegradation in air will take account of both primary and secondary processes, whereas for water the emphasis should be on the primary processes.

1.3. The Light Source

Although experiments made with natural light are the most relevant for photolysis studies, the meteorological conditions in most countries do not permit reproducible experimentation. In those countries where such experiments are possible, an exact description of test procedures is necessary.

The use of artificial light-sources eliminates the above-mentioned difficulty and has the additional advantage that it permits accelerated tests. A pre-requisite for the environmental relevance of an irradiation experiment is the practical limitation of the wavelengths in the incident light to values longer than 295 nm. (1), (2), (3), (4). In experiments with artificial light, the short wavelength cut-off edge in terms of a rate of attenuation as a function of wavelength should be defined (5), (6).

The relevance of model experiments does not depend on the spectral distribution of the incident light in so far as the above criterium is fulfilled. Any artificial polychromatic light source is acceptable when the spectral distribution and the intensity of the emitted light are known. However, the spectral distribution does matter if conjugation of different wavelengths is occurring. With conventional sources and the intensities generally used, annihilation between different excited states produced at different wavelengths

cannot be observed even in multi-component solutions. The only possible conjugation effect would be reactions between different radicals. Such processes are not expected in the photochemistry of a single molecule in the condensed phase, and they have not been reported and identified, up to now, in complex mixtures.

The type of sources used, the filters and the walls of the cells must satisfy the above criteria and must be precisely defined (cf. Appendix 1).

2. PHOTODEGRADATION IN AIR

2.1. Special Criteria for Air

Primary photodegradation in the gaseous phase can be observed even in the case of materials which have relatively low volatility. In a suitable experimental device, the substance is evaporated into air, illuminated in a photoreactor, and the unchanged compound and/or its photodegradation products are trapped and analysed. Experiments with and without irradiation yield information on the light-stability of the compound in the vapour phase. It should be noted, however, that wall reactions can play a very large part here, but this should not rule out the possibility of environmentally-relevant experiments. This effect can be investigated by comparing vessels with and without surface treatment. The photoproducts can also be isolated and identified in favourable instances. Reaction by secondary processes which may be initiated by trace compounds in the air must be avoided.

For photodegradation in the atmosphere, secondary photochemical reactions usually prevail over transformations of the molecule by photolysis (7). These reactions in the troposphere ($\approx$ 0-11 km) can be most complicated - the system propene, NO_x , air and light alone comprises more than 200 reactions (8). According to the present state of our knowledge there are essentially two species, the $\text{OH}^\bullet$ radical and ozone, which cause the degradation of an organic compound in the atmosphere by oxidation.

Of these oxidants the $\text{OH}\cdot$ radical is the more important reactant because of its high reactivity, whereas ozone reacts essentially with unsaturated systems (aromatic or olefinic compounds) at a comparable rate. Other radicals e.g. HO_2 and $\text{O}\cdot$ may also contribute but their quantitative effect is at present uncertain. Apart from the different mechanisms, the physical state of a substance has to be taken into account. Depending on vapour pressure, solubility and output to the environment a chemical can be monomolecularly dispersed in the troposphere; adsorbed or absorbed on aerosols; or exist as a homogeneous aerosol. The experimental approach must take account of this.

As has been shown by Hamaker (50) and Guth (51) a transport of less volatile chemicals from soil to the air is possible although in small amounts. A reverse transport of chemicals from the troposphere to other environmental compartments is also possible by dry deposition, absorption and solution in water, rainout and washout. Though the light-dependent reaction pattern of compounds which are monomolecularly dispersed in the atmosphere - for example low molecular weight hydrocarbons - has been well investigated by simulation experiments (9), (10), (11), (12), (13), (14), only a few studies of the photodegradation of aerosols exist (15), (16), (17). Aerosols are naturally released into the atmosphere in large quantities, and 10 to 15% of the total amount of aerosols may derive from human activities (18). Macroscopically they exist as dusts, smokes (solid) and fogs (liquid). Because of the specific physico-chemical state in which environmental chemicals are present in aerosols, data on the photodegradation of those chemicals in the aqueous, gaseous, adsorbed or solid phase can only give limited evidence on the specific photodegradation mechanisms of aerosols. Photodegradation of aerosols will not be considered in this report. It should be considered as a more sophisticated, multiphase form of photodegradation which depends on many other physical and chemical parameters.

Because secondary photochemistry is thought to prevail in the atmosphere, investigations must include more than just

the analysis of the reaction pattern of a compound under the action of light. Tropospheric conditions can be obtained in a simulation chamber. The experimental expenditure and the costs of such investigations, however, are so high that this method seems to be suitable only for projects of basic research. Nevertheless these investigations yield data and rankings of reactivity and degradability which can be used for the assessment of the relevance of screening or other less sophisticated tests. We do not know of any investigations of compounds of low volatility, or their aerosols, with regard to their photodegradation, possibly because they present physico-chemical and analytical difficulties compared to the highly volatile, classic components of the "Los Angeles Smog". However, this problem is currently being studied.

2.2. Review of Existing Methodologies for Air.

As will be shown below, the methods which were presented to the OECD have limited relevance to the environmental fate of chemicals in the air. However, more specific work is going on to develop model experiments which are relevant. Some published proposals will be discussed. Although some of them present theoretical as well as practical problems, they may be the nucleus from which adequate test protocols can be developed in the future.

2.2.1. Fujiki-test (19)

This test was proposed to the OECD as a screening test for photodegradation in the gas phase. It takes into account only the overall photodegradation without considering the generation and control of $\text{OH}^\cdot$ radical and O_3 concentrations, and can therefore be relevant only when direct photodegradation is predominant. The chemical under investigation is irradiated with UV-light in a relatively small reaction vessel. Wall reactions may play the most important part because of the large area-to-volume ratio of the reaction vessel. The light used contains wavelengths below 295 nm. This means that during

irradiations, primary photodegradation reactions will prevail which cannot occur in nature or, if they do, occur only above the troposphere ($\approx 15\text{--}50$ km). Irrelevant photochemical reactions may occur, varying according to the irradiating wavelengths and the quality of the air used. The purity of the carrier gas, which may influence the degradation of the reference chemical as well as the tested chemical, is not defined.

Deficiencies in the experimental methodology make the test appear unsuitable. The test is problematical with respect to its equipment, its handling and applicability. Only substances with relatively high vapour pressure can be tested. The concentration of the compound under investigation in the gaseous phase is not fixed but may have to be varied to allow for limitations in the analytical technique, and the volatility of the substance. Therefore the degradation rates of different chemicals cannot be compared, as the independence of the photochemical reactions on concentration is not proven.

2.2.2. GSF test (20)

The photomineralization test according to Korte and co-workers measures the total oxidation to CO_2 of organic compounds which are adsorbed on silica gel or sands and irradiated with light of wavelengths > 290 nm. The investigation of photo-reactions in an adsorbed (but not an actual aerosol) state represents only a special case of degradation processes occurring in the environment. For certain substances (e.g. particles of non-volatile chlorinated hydrocarbons in aerosols) it is necessary to have a photodegradation test where the chemical substance is present at a solid-gas interphase. It must be shown that the measured reactivity is environmentally significant.

The environmental relevance of the GSF photomineralization test remains questionable, all the more since we lack sufficient experimental data which could prove its relevance. It is not shown e.g. that it is representative for $\text{OH}\cdot$ radical photodegradation. Becker (55) and Klais (56)

have also shown that for some substances there are differences of several orders of magnitude between results from the photomineralisation test and those from tests more relevant to atmospheric conditions. The differences were attributed to the influence of surface reactions in the GSF test. A more theoretical objection is that we do not know the photomineralisation mechanism. To acquire a better understanding many more experiments are necessary, in which the nature of the intermediate photodegradation products should be identified.

The test description is, in its present state, insufficient. This resulted in rather large differences between the results in the OECD ring test programme, although the reproducibility in each laboratory was satisfactory. For the above reasons it is very doubtful that this test can be adapted so as to become adequately relevant, without major modifications.

2.2.3. Hendry proposal (42)

The main objective of the Hendry report is to develop two-tier test procedures for determining the importance of the three major chemical processes :

- direct photolysis,
- reaction with hydroxyl radicals,
- reactions with ozone.

- a) First tier. Hendry proposes as an initial step the calculation of **photochemical** degradation rates through semi-empirical models for primary and secondary photochemistry. An upper limit of the rate of direct photolysis is the rate of light absorption, computed in the gas phase and from the solar spectrum. The quantum yield of direct photolysis is then assumed to be unity for any absorbed wavelength .

The rate constant for the reaction with hydroxyl radicals is computed as an additive property. It is assumed that the rate constant of the reaction of the total molecule

with $\text{OH}^\bullet$ is the sum of rate constants for reactivities of each portion of the molecule (see Appendix 2). Four examples of such treatment are given in Hendry's report, in which two computed rate-constants k_{OH} are compared with the experimental values.

The additivity rule is generally not accepted in kinetics as little information exists on the reliability of such calculations. The degree of prediction decreases with increasing complexity of the compound under study, and verification of the calculated $\text{OH}^\bullet$ reactivity by measured reaction constants is not possible in the majority of such cases. The estimation of the rate constant for the reaction with ozone is based upon the same additivity rules (the molecular activity is the sum of the rate constant for each reactive group, i.e. double bonds, aromatic ring).

The method as proposed in the first tier by Hendry is unreliable because the theoretical prediction of quantum yield and rate constants is unrealistic, and the physical state of many compounds, eg. aerosol or dissolved in drops, makes the calculation questionable relative to the environmental situation.

b) Second tier. Hendry recommends that in a second tier the rate constants for the dominant processes are measured in more detailed model experiments. The quantum yield for primary photolysis is measured in a conventional mercury-free set-up for vapour-phase photochemistry. Monochromatic light and parallel beam are recommended but no precise description of the experimental device is given.

- $\text{OH}^\bullet$ Reactivity determination. In a 100 l. Teflon bag the compound under research and a reference compound are exposed to $\text{OH}^\bullet$ radicals which are generated by photolysis of HONO . This photolysis is carried out by fluorescent tubes or in sunlight. A relative method is proposed using different standards.

Nine reference compounds are listed (cf Table in Appendix 3).

The experimental procedure is quite complicated and only practicable in an experienced laboratory. Moreover, the method is only suitable for substances of relatively high volatility. Because the method has to be adapted to the substance under research in each case (suitable analytical device, suitable concentration range, suitable reference compound) a high expenditure of time and effort is necessary for each measurement.

- Ozone-reactivity determination. This determination is also carried out in a Teflon 100 l. bag, and the consumption of ozone is measured. In this case the objections mentioned for OH[•] reactivity determinations are also valid with respect to the high experimental expenditure and the limited applicability (only suitable for highly-volatile compounds).
- Calculation of lifetime. The "lifetime" τ (see Appendix 4 for general development) of the compound in environmental conditions can be computed. The experimental lifetime has to be recalculated to take into account the spectral intensity distribution of natural daylight (seasonal variations, latitude variations, etc).

The rate constants for the reaction with hydroxyl radical or with ozone give the corresponding lifetime if the hydroxyl radical or ozone concentrations are known under atmospheric conditions. Several paragraphs of the Hendry report are devoted to the determination of the OH[•] concentrations in polluted air or in the troposphere. Different methods of direct measurement of the OH[•] concentration are quoted (laser absorption spectroscopy, laser-induced fluorescence). Hendry reports the following data for OH[•] and O₃ concentrations:

- At ground level at mid-day in the highly-polluted troposphere the OH[•] concentration ranges from 2 to $8 \times 10^6 \text{ mol.cm}^{-3}$, whereas in the clean troposphere the range is 2 to $4 \times 10^6 \text{ mol.cm}^{-3}$.
- OH[•] concentration in the air decreases with increasing elevation by at least a factor of 10, from ground level

to the tropopause (0 to 15 km).

- At ground level the annually-averaged concentration of $\text{OH}^\cdot$ is 5 to $10 \times 10^5 \text{ mol. cm}^{-3}$.
- The best diurnal, seasonal, and elevation-averaged tropospheric concentration of $\text{OH}^\cdot$ is $4 \times 10^5 \text{ mol. cm}^{-3}$. In the northern hemisphere the best value is 2 to $3 \times 10^5 \text{ mol. cm}^{-3}$, and in the southern hemisphere the value is 4 to $6 \times 10^5 \text{ mol. cm}^{-3}$.
- A realistic tropospheric average for ozone is $1 \times 10^{12} \text{ mol. cm}^{-3}$ (40 ppb), the value being somewhat higher in the northern hemisphere and lower in the southern hemisphere. In polluted areas the ground-level concentration of ozone can easily increase to $4 \times 10^{12} \text{ mol. cm}^{-3}$ as a result of photochemical reactions of the higher concentration of hydrocarbons and nitrogen oxides which act as precursors of ozone.

2.2.4. ASTM proposed standard (22)

It is the purpose of this proposed standard to provide procedures for determining the rate constants for the transformation of chemical substances in the atmosphere resulting from photolysis or reaction with hydroxyl radicals or ozone. These rate constants are used to calculate the lifetimes of chemicals in the atmosphere with respect to these reactions. As the ASTM document is largely based on the above Hendry work, the comments already formulated on Hendry's proposal are also valid for the ASTM draft.

The ASTM Proposed Standard Practice is structured as a three-stage process, each stage or "Tier" involving the examination of three separate degradation pathways, as illustrated in the diagram below. Tier I involves estimating the rate of reaction with $\text{OH}^\cdot$ and O_3 by group additivity methods, and of photolysis rates (as upper limits) by assuming unit quantum efficiency (cf. Hendry) and a rate of reaction equal to the rate of light absorption (from the measured spectrum). Tier II involves the laboratory measurement of the three rates of reaction. Tier III involves the identification of the products of reaction in the three pathways.

Tier ↓	Reactant →	Ozone O_3	Hydroxyl Radical $OH^\cdot$	Actinic light $h\nu$
I		Theoretical rate estimation procedures		
II		Practical rate measurements with each of the reactants in question		
III		Characterisation of reaction products		

The ASTM document does not provide very clear criteria for deciding whether a compound should be tested in Tier I, II or III, or even whether it should be tested at all. Indeed, it expressly states that "Criteria for deciding whether to proceed from Tier I to Tier II are not defined in this standard practice". It is stated in Tier III, without giving further explanations, that the photoproducts of chemicals with very short lifetimes (one day or less) should be chemically characterised. At the end of the draft it is however stated that the problem of identifying reaction products is not straightforward.

2.2.5. Klöpffer proposal (24)

A proposal is made for a test in solution which simulates gas phase $OH^\cdot$ reactions. Experiments on the reaction of $OH^\cdot$ radicals with organic compounds in solution are easier to handle than experiments in the gas phase if a suitable $OH^\cdot$ radical source is available. $OH^\cdot$ radicals can be generated by irradiation of H_2O_2 , using "Fentons Reagent" (H_2O_2 , Fe^{++}) (52) or by radiolysis of H_2O (21). Comparative experiments with a set of chemicals resulted in smaller reaction constants in aqueous solution than in the gas phase, but both values were of the same order (see Appendix 5) (23),(24). Extreme care should, however, be taken if attempts are made to estimate aqueous-phase kinetics from gaseous-phase kinetics, and vice versa, as

no fundamental research results confirming an unambiguous correlation exist.

3. PHOTODEGRADATION IN WATER

3.1. Special criteria for Water

A clear distinction has to be made between photolability, i.e. the ease with which photochemical change can occur, and photochemical mechanisms that are a consequence of this photolability. The object of the test procedures should be to determine the photochemical lability of a chemical in water and to predict its lifetime in the aquatic environment, assuming that photodegradation is the rate-determining mechanism for its removal. A sequential testing procedure is necessary :

- Identification of concentration-independent photolability.
- Determination of environmental lifetime of a chemical in the aquatic environment if the rate-determining mechanism for its removal is photodegradation.
- Identification of the main stable photodegradation products whenever possible.

These steps are considered below.

3.1.1. The identification of concentration-independent photolability includes the recording of the absorption spectrum and the measurement of a relative rate of disappearance of the chemical. Any compound that has a molar extinction coefficient less than $1 \text{ Mol}^{-1} \text{ cm}^{-1}$ above 295 nm should be considered as non-photodegradable in this screening approach. Otherwise the relative rate of disappearance must be measured in relevant, simple but well-described equipment. The only prerequisite for the equipment is the cut-off of the radiation at below 295 nm and the overlap of the emission spectrum of the incident light and the absorption spectrum of the chemical.

The concentration, to be relevant, should be chosen according to the following criteria :

- It should be such that the photolysis mechanism is not concentration-dependent.
- The practical range of concentration will be determined by the lifetime of the chemical, by the environmental conditions likely in practice and the available analytical sensitivity.
- Because most actual environmental concentrations are rather low, the lowest practical concentration of the test substance should be used. The range of a few ppm is reasonable, because in most cases it is a starting point from which degradation rates can still be measured analytically even without the use of radioactively-labelled compounds. Radioassay methods facilitate analysis and simplify considerably the identification of the photoreaction products, if reference compounds are available.
- The isolation and identification of the photodegradation products require the use of rather more concentrated solutions. In most cases a material balance is impossible.

Practical considerations for meeting the above criteria are discussed below :

- Solutions should be prepared with twice-distilled water which has been well aerated, is sterile, held at a predetermined pH, and kept thermostatted. For chemicals of low solubility and when there is a need to characterise the photodegradation products it may be necessary to add a photochemically-inert organic co-solvent, e.g. acetonitrile, to solubilize both the test substance and its degradation products. Acetonitrile/water mixtures do not absorb significantly in the 300 nm region and also dissolve many water-insoluble substances to a sufficient extent. Acetonitrile at a concentration not exceeding 1% (v/v) is recommended.

It has been said (1) that compared with other co-solvents acetonitrile has little influence on the pattern of photodegradation products in water. On the other hand, as a consequence of the proportion of organically-bonded hydrogen which the mixtures contain, they simulate boundary

layer conditions of the kind which are often found in the environment , for example in oil films.

- The question of the environmental relevance of photodegradation experiments with a sensitizer is very controversial. It is possible that in the environment there are situations and conditions in which processes involving sensitisation take place, but it is very difficult to propose in a test method the use of a specific sensitiser, as these vary according to the chemical nature of the product being tested. It is preferred that photolysis tests be performed in "standardised" water.

With daylight as a light source, one or more reference compounds should be included and irradiated simultaneously with the test substance whenever photodegradation kinetics are being determined, in order to obtain degradation rates which are intercomparable. With artificial light-sources, in order to obtain more information about photokinetics, actinometers should be used in parallel with the investigation of the photolysis of the chemical (use of a carousel). Darkened control experiments must also be included in order to detect side-effects, such as non-light-dependent effects and reactions.

- 3.1.2. The second step involves testing procedures which give quantitative data more relevant to the environmental fate of the chemical eg. molar extinction coefficients and mean quantum yields, from which an environmental lifetime can be calculated.
- 3.1.3. In the third step the main photoproducts which are not photodegradable should be chemically characterised, and when possible identified, using classical physico-chemical and/or analytical methods. The further assessment of these photoproducts will be a function of the possible environmental impact. The experimental methodology will be adapted to be as relevant as possible to the environmental conditions.

3.2. Review of Existing Methodologies for Water

The purpose of this section is to review critically the test methods as proposed by EPA (25), ASTM (26) and in a Battelle Report (27). The Zepp et al (28), (29), (30) publications were consulted as a help in establishing a relevant methodology.

3.2.1. E.P.A. test (25)

The procedure proposed by the EPA is designed to test the stability of light-absorbing chemical constituents in surface water. The aim of the test is to determine rate constants and half-lives for the direct photolysis of chemicals in aqueous media ("pure water", term used by EPA). It is open to serious criticism on a number of points.

- a) The light source suggested is sunlight, and reference compounds are used as chemical actinometers. In those tests where the photochemically-significant wavelengths are greater than 330 nm, then satisfactory control conditions and test reproducibility could be established, leading to results independent of geographic location, season and operator. Where the compound under test has all of its absorption below 330 nm, problems will most certainly arise due to the transmission characteristics of the glass tubes used, the emission cut-off characteristics of daylight in the ultraviolet, and the light absorption characteristics of the chemical actinometer, particularly where rapid changes in absorption can compensate for equally rapid falls in available ultra-violet over short wavelength intervals.
- b) Sample purity/Limiting molar extinction coefficient (ϵ). There is a problem associated with sample purity and the recommended lowest molar extinction coefficient of any samples to be tested. If samples for testing satisfy the criterion that the molar extinction coefficient must exceed $0.1 \text{ M}^{-1} \text{ cm}^{-1}$ at any wavelength above 290 nm, and sample purity must exceed 99%, the situation can arise where a sample containing a minor impurity but with a

molar extinction coefficient exceeding 10,000 satisfies the condition for testing.

$$\begin{array}{ll} \text{i.e. Pure sample, 100\%} & \epsilon > 0.1 \text{ M}^{-1} \cdot \text{cm}^{-1} \\ \text{Sample, 99.9\% + 0.1\% Impurity} & \epsilon = 0.1 + 0.001 \times 10^4 \\ & = 10 \end{array}$$

$$(M = \text{mole.liter}^{-1})$$

Most chemicals of commercial origin, even after purification, would fall into the category for testing solely on the basis of the impurity content. Meaningful tests would be impossible since all our efforts would in fact result in testing the photochemical stability of a minor component. Thus a definition of chemical purity is not in itself sufficient and must be supplemented by an optical purity. i.e. the impurity level must be so low that it no longer influences the absorption spectrum.

- c) Pure water as solvent would give a pH limited by the concentration of carbonic acid (dissolved CO_2), which could give misleading results relative to environmental surface water, particularly where acids or bases are being tested or are the primary photo-products.
- d) Specifying an upper concentration of less than 10^{-5} M , and an optical density not exceeding 0.02 would probably make simple monitoring of photodegradation by spectral absorption possible on only the most sophisticated of absorption spectrophotometers e.g. a test compound would require a molar extinction coefficient of greater than 2000. This condition would ensure that chemicals with molar extinction coefficients approaching the lower limit of $0.1 \text{ M}^{-1} \text{ cm}^{-1}$, and in concentrations less than 10^{-5} M , would have optical densities never exceeding 0.000001. The limitation of the optical density to 0.02 will otherwise decrease proportionally the concentration in the test solution with increasing molar extinction coefficients (e.g. concentration of 10^{-6} M for a molar extinction coefficient of 20,000).

- e) The reaction tubes recommended by EPA are of glasses which are unsatisfactory because of the UV cut-off, and tendency to solarize. The concentration limits imposed by the limited volume (11 cm³) of aqueous test solution impose serious restrictions on the choice of analytical techniques suitable for a certain degree of precision. Thus, any attempt to use 10 cm path-length cells in order to obtain elevated optical density would require cuvettes with volumes greater than 11 cc.

3.2.2. Standard proposed by ASTM working group (26)

This standard, which has not been approved by ASTM, contains procedures for obtaining information on photolysis rates, quantum yields and phototransformation products of chemicals in an aqueous environment. A three-tiered approach, becoming more mathematical up to tier 3, is proposed. The document is clearly a guideline paper, leaving a certain liberty in the choice of the details of the experimental methods. ECETOC fully supports this approach, taking into account that the criteria put forward by Good Laboratory Practice will also be applicable. A number of criticisms, however, can be made.

- a) The document specifies the use of borosilicate glass on several occasions without mentioning the change in the spectral transmission of this material as a consequence of solarization. It is essential that the user of the method should be fully aware of the difficulties in the use of any transparent material other than optical quartz, and the description should include guidance on the selection and checking both of the filters and reaction vessel materials.

The use of laboratory light sources as a substitute for sunlight, which will be almost a sine qua non in more northerly latitudes, is not adequately specified.

- b) In paragraph 7.5, although it is true that "the rates of photochemical reactions are not thought to be affected

to any appreciable extent by changes in temperature", the rates of reactions as a direct consequence of photo-activation may be greatly affected by temperature. This should be made clear.

- c) It is questionable whether a precise requirement for 5 days exposure in natural sunlight is relevant. The exposure period in natural sunlight will be defined by the lifetime of the chemical. The statement in par.8.2.1. that the method is usable only from March to September underlines the importance of using artificial light sources as an alternative to natural sunlight.
- d) The procedure whereby environmental lifetime is predicted from the measured absorption spectrum in aqueous solution, together with the measured quantum yield, is acceptable provided that it is based on sound data.

3.2.3. Battelle report (27)

The purpose of this was to collect information on the rate constants and half-lives of photo-activated reactions of a set of organic chemicals of specific interest to the Office of Toxic Substances, US Environmental Protection Agency.

- a) The arguments against the relevance of photosensitized degradation advanced on section 3.1.1. of their report are valid only if oxygen deactivates the excited state of the sensitizer without producing further reactive molecules.
- b) Use of the gas-phase spectrum to estimate the aqueous solution spectrum is admissible only as a last resort and for non-polar compounds (cf. section 2.2.5. of this report and Appendix 5).
- c) The report makes the important point that OH[•] radical reactions may play an important part even in aquatic systems. From the environmental point of view this che-

mistry has not been investigated as extensively in water as in air, and may require further research.

3.2.4. General comments

For the legislative requirements as mentioned in the beginning of the Summary, the ASTM proposal could be a starting-point for developing a future methodology regarding photodegradation in water. The ASTM proposal needs to be adapted to meet the criticisms and criteria as above before it becomes relevant to the reaction under environmental conditions.

4. PHOTODEGRADATION ON SOIL

4.1. General Discussion

For a general industrial chemical which may appear on soil and does not biodegrade, or is not eliminated by any abiotic route of degradation such as redox and hydrolysis reactions, a photodegradation test could be suggested although it is the least likely way of elimination. An assessment should be made as to whether there is any transport from the soil either to water or to the air, where the chemical could more easily photolyse. Knowledge of the soil/air distribution coefficient should indicate whether a chemical partitions to a considerable extent into the soil and thus whether degradation in soil could be a relevant route of elimination.

The soil/air distribution coefficient can be calculated from other coefficients (50) (51) and is defined as

$$\frac{C_{\text{soil}}}{C_{\text{air}}} = \frac{C_{\text{water}}}{C_{\text{air}}} \cdot \left(\frac{1}{r} + k \right)$$

The water/air distribution coefficient can be calculated from the following equation :

$$\frac{C_{\text{water}}}{C_{\text{air}}} = \frac{\text{S.R.T}}{p \cdot M_w \cdot 10^6}$$

where

C_{soil} = concentration of chemical ($\mu\text{g.g}^{-1}$) in wet soil, on a dry weight basis.

C_{air} = concentration of chemical in air ($\mu\text{g.cm}^{-3}$)

C_{water} = concentration of chemical in water ($\mu\text{g.cm}^{-3}$)

r = weight of soil per unit weight of water

k = soil/water adsorption coefficient ($\mu\text{g/g}^{-1}$)

S = water solubility ($\mu\text{g.cm}^{-3}$)

R = gas constant, 8.29×10^6 ($\text{Pa.cm}^3.\text{K}^{-1}.\text{mol}^{-1}$)

T = absolute temperature ($^{\circ}\text{K}$)

p = vapour pressure (Pa)

M_w = molecular weight (g.mol^{-1})

Measured soil/air distribution coefficients of some pesticides range over several orders of magnitude, up to values of 10^8 (31). In a model experiment on specified soil types, with 12% moisture and a gas flow-rate of 30l.h^{-1} , a $C_{\text{soil}} / C_{\text{air}}$

distribution coefficient of 5×10^6 was found (51). This results in a loss at 35°C of 1.5% of chemical per day for a sandy soil (type, Collombey-Switzerland) and in a loss of 0.5% of chemical per day for a silty loam (type, Les Evouettes-Switzerland). These results were obtained with a soil which was sterile and without vegetation.

Only when it is proved that no translocation of the chemical from soil to air or water is taking place should a photolysis test on soil be considered.

4.2. Review of Existing Methodologies for Soil

The existing methodology for studying photodegradation of pesticides on soil surfaces has been recently reviewed (53), (54). Although experiments on photolysis on soil surfaces are required by some registration authorities (32), published information is limited (32 to 38). Some of the studies referred to were carried out in natural sunlight (33,34,37,38) and depended strongly on the meteorological variations of the environment. In others, mercury vapour arcs were used

(36,37) which obviously showed spectral energy distributions different from those of sunlight. The irradiation of materials on silica gel, soil, leaf surfaces or glass plates is described in the literature for the measurement of photodegradation of pesticides on surfaces (20) (37) (39) (40). Silica gel has the advantage that a quantitative and qualitative thin-layer chromatographic analysis can easily be carried out after illumination, but the environmental relevance of such a test is very debatable because of the high surface activity and the acidic properties of the silica gel, which often lead to decomposition even in the dark. Modifications of the UV absorption and emission spectrum of a substance during interaction with silica gel are also known (41), and photochemical surface reactions can also occur. A procedure more truly representative of the environmental situation, but which is more tedious and has greater analytical difficulties, is the illumination of material which has been incorporated into soil at concentrations approximating to actual practice. Thin layers should be used when working in soil, because the soil itself strongly absorbs light. Occasional moistening may accelerate photodegradation.

D. GUIDELINES FOR RELEVANT METHODOLOGIES

Considering the criteria which must be fulfilled, it is highly improbable that "screening" tests which are both simple and relevant can be developed for air and soil. For testing chemicals which may occur in significant amounts, protocols which are more environmentally-relevant will have to be used but these will inevitably be more elaborate. In this chapter some basic principles are laid down, and proposals are made, for the future development of practical tests applicable for legislative submissions.

1. PHOTODEGRADATION IN AIR

1.1. Theoretical

The need to carry out a photodegradation test at all will

depend on the potential release rate and tonnage, and on a possible effect on the environment. The occurrence of a chemical in the atmosphere is not relevant until its level, or that of one of its degradation products, reaches a significant value relative to the naturally-occurring level of that material. The possibility that a product of short lifetime gives an intermediate degradation product of long lifetime is also relevant here.

The following relevant factors should be taken into account in any proposed test methods.

- 1.1.1. The test method should be capable of giving results from which an assessment can be made of the potential hazard from the photodegradation of airborne chemicals. For example the test method should be capable of revealing, among other things, a potential to cause photochemical smog under conditions of elevated levels of ozone and/or other photochemical oxidants. This will be indicated by a short lifetime (Appendix 4) in the lower troposphere combined with specific physical properties (eg. volatility); a release quantity and rate of a certain order of magnitude; and a release pattern which leads to elevated local concentrations. In considering these three factors the meteorology of the place of release is also relevant.
- 1.1.2. It is accepted that the experimental determination of τ for reactions with $\text{OH}\cdot$, and the direct photodegradation, will be accelerated in the test, but the decay mechanism must be comparable with the chemical pathway occurring in the environment.
- 1.1.3. Primarily, the test must determine the tropospheric lifetime under internationally-agreed standard conditions, eg. $T = 265^\circ\text{K}$, $\text{OH}\cdot = 4 \times 10^5 \text{ molecules/cm}^3$, or some other accepted set of conditions to which all measurements should be normalized. Correspondingly-accepted parameters should be used in quoting primary photodegradation rates. Since the percentage of a tropospheric pollutant entering the stratosphere, and hence the possibility of ozone perturbation

or greenhouse effect, depends on the tropospheric lifetime the test must be applicable to substances with very long tropospheric lives, and must be able to discriminate between these long lifetimes. The existence of so many parameters which have to be considered does not permit the elaboration of a simple test protocol. As photodegradation in air is the most important, and at the same time the most complex, of all photodegradation phenomena, the development of the proposed test methodology will require more practical work.

1.2. Test Methodology - Predictive

1.2.1. Lifetime

The rate of $\text{OH}\cdot$ reactions with a test compound, and hence the lifetime, can be crudely estimated by eg. the method of Hendry (21) used by the ASTM (22), provided that sufficient relevant, experimentally-determined data on similar compounds are available as a basis for the prediction, eg. experimentally-determined $\text{OH}\cdot$ reaction rates for neighbouring members of a homologous series which includes the compound for which the prediction is required. It is emphasised again that the calculated data for the lifetime have only a predictive value. The accuracy of prediction decreases with the increasing complexity of the test chemical.

1.2.2. Photochemical breakdown rate

It is considered that the prediction of a photochemical breakdown rate based on the absorption spectrum, and a quantum yield assumed equal to unity, is not meaningful.

1.3. Test Methodology - Experimental

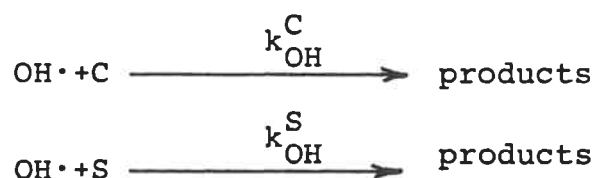
The known chemical processes occurring in air photodegradation i.e. direct photolysis, reaction with $\text{OH}\cdot$ and reaction with O_3 , must be independently tested. The reaction with hydroxyl radical is at present assumed to be the most important.

1.3.1. Determination of primary photodegradation lifetime.

The lifetime can be computed mathematically (see Appendix 6) after experimental determination of the absorption spectrum, the intensity of the incident light and the quantum yield of disappearance of the compound.

1.3.2. Determination of secondary photodegradation ($\text{OH}\cdot$ and O_3 reactivity). For determining $\text{OH}\cdot$ reaction-rates the most-used method is that of Cox (45) in which $\text{OH}\cdot$ is produced from HONO. Other methods to produce $\text{OH}\cdot$ radicals may be suitable, such as those of Clyne (46) (47), Pitts (8) and Zellner (48). For measuring the $\text{OH}\cdot$ reactivity, Cox proposes the use of a set of fluorescent tubes emitting at 365 nm. By photolysis of HONO at about 365 nm a high stationary concentration of $\text{OH}\cdot$ is supplied (higher than the environmental concentration), and the primary photochemistry can be neglected compared with the $\text{OH}\cdot$ reaction, which is the main disappearance process (a check of the direct photolysis of the compound at 365 nm has to be carried out).

With standards of known reactivity (21), only the ratio of the rate (R) of disappearance of the compound (C) under study to the rate of disappearance of a standard (S) is needed.



$$R_{\text{C}} = k_{\text{OH}}^{\text{C}} [\text{OH}\cdot] [\text{C}] = - \frac{d\text{C}}{dt} \quad \text{which after integration}$$

$$\text{gives} \quad \text{Log} \frac{[\text{C}]_0}{[\text{C}]_t} = k_{\text{OH}}^{\text{C}} [\text{OH}\cdot] \cdot t_{\text{irr}}$$

$$\text{In the same way} \quad \text{Log} \frac{[\text{S}]_0}{[\text{S}]_t} = k_{\text{OH}}^{\text{S}} [\text{OH}\cdot] \cdot t_{\text{irr}}$$

$$\text{so that} \quad \text{Log} \frac{[\text{C}]_0 / [\text{C}]_t}{[\text{S}]_0 / [\text{S}]_t} = \frac{k_{\text{OH}}^{\text{C}}}{k_{\text{OH}}^{\text{S}}}$$

Zellner (47) uses static flash-photolysis to generate $\text{OH}\cdot$ radicals from H_2O , followed by measurement of the decay of the $\text{OH}\cdot$ radical concentration in the presence of excess test substance, as measured by OH resonance absorption.

For measuring O_3 reactivity, the ozone reaction constant k_{O_3} is obtained by kinetic treatment of the disappearance of the chemical or ozone, in a mixture of the chemical with ozone and pure air as diluent. The ozone reaction constants are then calculated according to a pseudo-first-order reaction (cf Appendix 7).

1.3.3. Apparatus

The same apparatus can be used for testing the primary photochemistry and the reactivity with $\text{OH}\cdot$ and O_3 , as follows.

Irradiation chamber : a polytetrafluoro-ethylene bag of 100 to 200 liters, and a wall thickness of about 2 mm.

Light sources : to avoid heterogeneity in the chamber (light zones vs dark zones) the incident beam must cover the whole surface of the irradiation chamber. It is then necessary to use fluorescent tubes in large numbers with two types of tube disposed symmetrically around the chamber, i.e.

- n (for example 4) tubes emitting around 310 nm, eg. WESTINGHOUSE FS 20W T12 or Philips TL20/12 with the necessary filters ($\lambda_{\text{max}} = 310 \text{ nm}$; spectral width $\approx 60 \text{ nm}$).
- n tubes emitting around 365 nm, eg. Philips TL20/05 or Mazda TFWN 20-40 ($\lambda_{\text{max}} = 365 \text{ nm}$; spectral width $\approx 60 \text{ nm}$).

Vacuum set-up : mercury and grease free; down to 10^{-6} mm Hg .

Nitrous acid generator : for producing $\text{OH}\cdot$

Ozone generator

Ozone monitor : measurement of O_3 concentration at zero

time and during reaction, by means of chemiluminescence for example.

Analytical device : measurement of the rate of disappearance of the studied compound and reference compound.

2. PHOTODEGRADATION IN WATER

2.1. General Considerations

A complete study of the photodegradability of a compound in aqueous solution must take in account the following three stages :

- a determination of the lifetime of the compound under polychromatic irradiation in dilute and aerated solution. These kinetic data can generally be measured only at the first step of the primary photoreaction (degree of conversion lower than 0.25);
- an analytical study of this step leading to the identification of photoproducts ;
- an analysis of the secondary photoreactions. Two approaches of different complexity might be proposed, ie. a check whether UV-absorbing photoproducts accumulate under prolonged irradiation, or a full kinetic analysis of each photoproduct.

Only a proposed methodology for determining the lifetime of a photodegradable compound (first of the above stages) is given here, because the second and third stage experimentation will be determined by the nature of the chemical, its mode of breakdown, the breakdown products and their biodegradability etc. These stages are largely a question of appropriate analyses. As more experience is gained about photoreactions in aqueous solution a more detailed methodology can be developed, but will need more practical work.

2.2. Experimental Methodology

The lifetime of a photodegradable compound excited under

polychromatic light in solutions of low absorbance (low optical density) can be computed from the same kinetic equation as for primary photodegradation in air (see Appendix 6) and is based upon the measurement of the molar extinction coefficient ϵ , the actinometric measurement of the intensity of the incident light $I_{oi}(\lambda)$ and the quantum yield of disappearance $\phi(\lambda)$.

- 2.2.1. The molar extinction coefficient, $\epsilon(M^{-1}.cm^{-1})$ is determined from the absorption spectrum recorded on conventional spectrophotometers. For the best accuracy, absorbance is measured in the range 0.3-0.8. The molar extinction coefficient is computed from Beer-Lambert's law :

$$D(\lambda) = \epsilon(\lambda) \cdot [P] \cdot \ell$$

with $D(\lambda)$ the absorbance or optical density at wavelength λ
 $[P]$ the concentration in M ($M = \text{mole.liter}^{-1}$)
 ℓ the optical path in cm.

- 2.2.2. Measurement of intensity of incident light $I_{oi}(\lambda)$.
 The spectral distribution of incident daylight $I_o(\lambda)$ is usually known and is expressed in $\text{einstein.cm}^{-2}.\text{sec}^{-1}$. With artificial light supplied by source and filters it is necessary to use solutions of actinometers. All the incident light must be absorbed by the actinometer. Work at high absorbance ($1 < D < 2$) is recommended to avoid the necessity for the measurement of optical path. Work at very low absorbance, i.e. at very low concentration of actinometers, is not recommended since the photochemical process upon which actinometry is based is not necessarily monomolecular (Appendix 8).

- 2.2.3. Measurement of quantum yield of disappearance $\phi(\lambda)$. The most simple and accurate determination of a quantum yield is carried out in parallel monochromatic light. When reasons others than scientific make necessary the use of polychromatic light, accuracy and simplicity decrease with an increase of the band width. The quantum yield of disappearance of the compound is measured from the experimental

rate of disappearance R (in $M.s^{-1}$) and from the computed absorbed intensity

$$\int_{\lambda_1}^{\lambda_2} I_a(\lambda) . d\lambda \text{ (in einstein.l}^{-1}.s^{-1}) :$$

$$\phi = \frac{R}{\int_{\lambda_1}^{\lambda_2} I_a(\lambda) . d\lambda}$$

For measuring ϕ , the best accuracy is obtained in parallel beam (the optical path l is known without integration), and for solutions with absorbance in the range 0.1-1 (Appendix 9).

2.2.4. Computation of τ in the environment.

Data on daylight allow calculation of the absolute number of incident photons in each spectral range. The lifetime is deduced from (see Appendix 6) :

$$\tau = \frac{1}{2300 \int_{295}^{450} \phi(\lambda) . I_{01}(\lambda) . \epsilon(\lambda) . d\lambda}$$

The integral is computed as a sum by the technique described previously (split into 20 nm width spectral ranges, cf Table 1, Appendix 8).

2.2.5. A practical example, ie. the determination of the lifetime of 4-nitrophenol in water, is given in Appendix 10.

3. PHOTODEGRADATION ON SOIL

A simple method has been described by Burkhard and Guth (39) which gives some information on the expected rate and pathway of breakdown of a chemical in the soil, under the influence of light. However, because of the many different, sometimes unknown, parameters which can interfere in soil photolysis (type of soil, water-content, presence of inorganic salts and organic compounds etc.) no general methodology can be recommended at present. According to the situation, the methods described in the literature may be adapted so as to be as relevant as possible to the real environmental situation.

E. RECOMMENDATIONS

1. Further work should be carried out to elaborate relevant, repeatable and cost-effective test methods for the assessment of the photodegradation of chemicals in the environment (air and water).
2. The work on photodegradation in air should start with the development and validation of methods for assessing the homogeneous photoreaction with $\text{OH}\cdot$ radicals, and with ozone, followed by a method for the primary photodegradation. A test method for determining the atmospheric lifetime of a chemical should also be developed and validated. This will involve practical work based on the principles laid down in this report, and tests in various laboratories.
3. A number of laboratories should test the method proposed by the Laboratoire de Photochimie of the University of Clermont-Ferrand for the measurement of primary photodegradation of chemicals in the aqueous phase. This method involves a standardised apparatus which is in accordance with the principles set out in this report.

F. APPENDICES

APPENDIX 1 : LIGHT SOURCES AND CELLS

The light source can emit either a continuous spectrum (Xenon high-pressure lamps, fluorescent tubes) or a predominantly line spectrum (mercury high-pressure arcs). Xenon sources are generally recommended. This is not because they give a better simulation of the sun or daylight, but because they are more convenient to correct for the photon-intensity distribution. This permits a comparison of results obtained with different light sources.

Filters to correct the wavelength are often made of borosilicate glass. It must be noted that the commercially-available glasses differ slightly in their transmission characteristics, and some even age towards a cut-off at longer wavelengths after even brief exposure to light ("solarization"). Thus optically-stable filters are preferred.

The measurement of UV intensities in daylight or from solar simulators should not be undertaken with UV-extended silicon photodiodes unless very high-quality filters are used that efficiently block all other wavelengths at least to 1 μm , with an overall attenuating efficiency of 10^6 .

The walls of the cell can be made of the same borosilicate glass, or of quartz. The combination of lamp(s) and filter(s) must be designed to maintain a constant power-distribution spectrum, with the above-mentioned criteria. Two technical solutions are possible : either standardizing the whole irradiation device, or determining the absolute values of the photons absorbed in every spectral range (i.e. measuring quantum yields).

APPENDIX 2 : CALCULATION OF OH· RADICAL REACTION RATE CONSTANTS
ACCORDING TO HENDRY (42)

The rate constant for the reaction with hydroxyl radicals is computed as an additive property. It is assumed that the rate constant of the reaction of the total molecule with OH· is the sum of rate constants for reactivities of each portion of the molecule.

$$K_{OH} = \sum_{i=1}^i n_i \cdot \alpha_{H_i} \cdot \beta_{H_i} \cdot k_{H_i} + \sum_{j=1}^j n_j \cdot \alpha_{E_j} \cdot k_{E_j} + \sum_{\ell=1}^{\ell} n_{\ell} \cdot \alpha_{A_{\ell}} \cdot k_{A_{\ell}}$$

The first term corresponds to the abstraction of hydrogen atoms (k_{H_i} is the reactivity of i^{th} hydrogen atom which depends on the degree of substitution on the adjacent atom; α_{H_i} and β_{H_i} account for the effects of substitution respectively in the α and β positions; n_i is the number of equivalent hydrogen atoms).

The second term corresponds to the addition to a double bond (k_{E_j} is the reactivity of the j^{th} carbon atom double bond, and α_{E_j} is taken as unity except when a hydrogen atom is attached to the double bond); n_j accounts for the repetition of each unique double bond.

The third term corresponds to addition to aromatic rings ($k_{A_{\ell}}$ is the reactivity of the ℓ^{th} aromatic group; $\alpha_{A_{\ell}}$ accounts for the effects of halogen atom on the ring).

The different rate constants k_{H_i} , k_{E_j} , $k_{A_{\ell}}$ and the corrective factors have been determined in preliminary experiments on typical compounds (methane, ethane, ethylene, benzene.....)

APPENDIX 3 : k_{OH} REACTION CONSTANTS OF REFERENCE
COMPOUNDS (HENDRY (42))

	<u>$k_{OH} \text{ (cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)}$</u>
methane	$= 9.5 \times 10^{-15}$
1,1,1-trichloro-ethane.....	$= 1.5 \times 10^{-14}$
chloroform	$= 1.0 \times 10^{-13}$
ethane	$= 2.9 \times 10^{-13}$
benzene	$= 1.2 \times 10^{-12}$
toluene	$= 6.4 \times 10^{-12}$
ethylbenzene	$= 7.9 \times 10^{-12}$
n-xylene	$= 2.06 \times 10^{-11}$
2-methylbutene	$= 8 \times 10^{-11}$

APPENDIX 4 : CALCULATION OF LIFETIME IN AIR

The lifetime of a chemical compound in environmental conditions can be computed as

$$= \frac{1}{k_{\text{OH}} [\text{OH}]_{\text{env}}} + \frac{1}{k_{\text{O}_3} [\text{O}_3]_{\text{env}}} + \frac{1}{2300 \int_{\lambda_2}^{\lambda_1} \phi(\lambda) \cdot I_{\text{oi}}(\lambda) \cdot \epsilon(\lambda) \cdot d\lambda}$$

where :

k_{OH} and k_{O_3} = the bimolecular rate constants for reactions with $\text{OH}^\bullet$ and O_3 .

$[\text{OH}^\bullet]_{\text{env}}$ = environmental stationary concentration of $\text{OH}^\bullet$ radicals
(4×10^6 to 10^7 molecules/cm³ (45); 4×10^5 molecules/cm³ (42)).

$[\text{O}_3]_{\text{env}}$ = environmental stationary concentration of ozone
(7.3×10^{11} molecules/cm³ (45); 10^{12} molecules/cm³ (42)).

Usually the first term is predominant, and

$$\tau \approx \tau_{\text{OH}^\bullet} = \frac{1}{k_{\text{OH}^\bullet} [\text{OH}^\bullet]_{\text{env}}}$$

$\int_{\lambda_2}^{\lambda_1}$ = integration over the absorption band(s) of the chemical.

$\phi(\lambda)$ = quantum yield of disappearance under excitation at λ (nm)
 ϵ = molar extinction coefficient at λ (nm), ($\text{M}^{-1} \text{cm}^{-1}$).
 $I_{\text{oi}}(\lambda)$ = spectral distribution of daylight ($\text{einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$).

The lifetime at 265°K is thus directly derived from the measured rate constant and a conventionally-accepted value of $\text{OH}^\bullet$ environmental concentration (4×10^5 molecule/cm³). As example, $\text{CH}_3\text{-CCl}_3$ would yield a $\tau = 6$ years under these conditions, while $\text{CH}_2=\text{CHCl}$ would give a $\tau = 7.2$ days.

APPENDIX 5 : COMPARISON OF BIMOLECULAR REACTION CONSTANTS k_{OH} IN AIR AND WATER ($M^{-1}.s^{-1}$) (23) (24) .

N°	Substance	$\log k_{OH}$ water (23)	$\log k_{OH}$ air (24)
1	benzene	9,56	8,95
2	chloroform	6,93	7,78
3	p-cresol	10,08	10,49
4	ethanol	9,02	9,28
5	ethyl acetate	8,38	9,06
6	methanol	8,71	8,78
7	propanol	9,18	9,51
8	n-propyl acetate	8,91	9,41
9	toluene	9,48	9,52
10	methyl ethyl ketone	8,73	9,32
11	tetrahydrofuran	9,20	9,95
12	methyl acetate	7,85	8,04
13	methyl propionate	8,43	8,23
14	ethyl propionate	8,72	9,03
15	1,2-epoxybutane	8,65	9,16
16	epoxypropane	8,15	8,89
17	diethyl ether	9,37	9,73
18	nitromethane	8,28	8,81

APPENDIX 6 : DETERMINATION OF PRIMARY PHOTODEGRADATION
LIFETIME.

The lifetime can be computed from the equation :

$$R = - \frac{d[P]}{dt} = \int_{\lambda_1}^{\lambda_2} \phi(\lambda) \cdot I_a(\lambda) \cdot d\lambda, \text{ where :}$$

$\phi(\lambda)$ is the quantum yield of disappearance of the chemical.

$I_a(\lambda)$ is the absorbed intensity expressed in $\text{einstein.l}^{-1}.\text{s}^{-1}$ (l=liter) in the spectral range (λ_1, λ_2) . This range is defined as overlap of the incident light and the absorption spectrum of the compound.

At low absorbance ($D < 0.02$) in the unit volume (1 liter)

$$I_a(\lambda) = \frac{1000}{l} I_{oi}(\lambda) \cdot (1 - 10^{-\epsilon \cdot [P] \cdot l})$$

$$I_a(\lambda) = 2.300 \cdot \epsilon(\lambda) \cdot [P] \cdot I_{oi}(\lambda)$$

$I_{oi}(\lambda)$ = intensity of incident light in $\text{einstein.cm}^{-2}.\text{s}^{-1}$

$\epsilon(\lambda)$ = molar extinction coefficient ($\text{M}^{-1}.\text{cm}^{-1}$)

l = optical path in cm.

$[P]$ = concentration of chemical P in mole. per liter

$$\text{Then, } - \frac{d[P]}{dt} = 2300 P \int_{\lambda_1}^{\lambda_2} \phi(\lambda) \cdot I_{oi}(\lambda) \cdot \epsilon(\lambda) \cdot d\lambda$$

The e^{-1} lifetime τ , defined from the relation $[P] = [P_0] e^{-t/\tau}$, may be computed as

$$\tau = \frac{1}{\int_{\lambda_2}^{\lambda_1} \phi(\lambda) \cdot I_{oi}(\lambda) \cdot \epsilon(\lambda) \cdot d\lambda}$$

Experimental determination of $\epsilon(\lambda)$, $I_{oi}(\lambda)$ and $\phi(\lambda)$ is thus needed. $\epsilon(\lambda)$ is determined from the absorption spectrum recorded on conventional spectrophotometers.

The molar extinction coefficient is computed from the generally-obeyed Beer-Lambert law :

$$D(\lambda) = \epsilon(\lambda) \cdot [P] \cdot l$$

$D(\lambda)$ is the absorbance or optical density at a wavelength λ .

The spectral distribution of incident daylight $I_{oi}(\lambda)$ is usually known. For experiments in the gas phase with artificial light it is necessary to use chemical actinometers. As in this case the optical path is not determined by the geometry of the sources and irradiation chamber, it is necessary to measure directly the absorbed intensity. It is recommended to use monochromatic light (e.g. a set of fluorescent tubes emitting at 310 nm). The actinometer must be used at the same absorbance at 310 nm as the compound under investigation. Contrary to the techniques used in solution, actinometry in the gas phase is not so well developed. The quantum yield of disappearance ϕ of the compound is measured from the experimental rate of disappearance R (in $M.s^{-1}$) and from the absorbed intensity I_a (in $einstein.l^{-1}.s^{-1}$)

$$\phi = \frac{R}{\int_{\lambda_2}^{\lambda_1} I_a(\lambda) . d\lambda}$$

This quantum-yield determination should consist of a series of individual determinations across whatever absorption range the substance possesses. This will be experimentally very difficult if the yield and the extinction coefficient are small. A method for the determination of the quantum yield, extending across that part of the material's absorption spectrum lying within the range of tropospheric solar radiation and revealing the wavelength-dependence of quantum yield cannot be defined in general, but must be individually tailored to each product.

APPENDIX 7 : DETERMINATION OF OZONE REACTION RATE CONSTANTS
AND LIFETIME

In the atmosphere; where the reaction



occurs, the decay of the chemical is given by

$$-\frac{d[P]}{dt} = k_{O_3} [O_3] [P] \quad (A)$$

with k_{O_3} the reaction constant, in $M^{-1}.s^{-1}$,

and $[O_3]$ = the concentration of O_3 in M. ($M = \text{mole.liter}^{-1}$)

$[P]$ = the concentration of the chemical in M.

As $[P] \gg [O_3]$ and $[O_3]_{t=0} \approx 1 \times 10^{15} \text{ M (40 ppb)}$

we have
$$-\frac{d[O_3]}{dt} = k_{O_3} \cdot [O_3] \cdot [P] + k_w \quad (B)$$

where k_w represents the reaction constant of the reaction



As the test compound concentration $[P]$ remains essentially constant, the equation (B) may be rearranged to yield

$$-\frac{d \ln [O_3]}{dt} = k_w + k_{O_3} \cdot [P]$$

k_w may be determined from an experimental decay rate in the absence of the chemical and permits a determination of k_{O_3} . The lifetime τ_{O_3} is given by

$$\tau_{O_3} = \frac{1}{k_{O_3} \cdot [P]}$$

APPENDIX 8 : ACTINOMETRY IN THE AQUEOUS PHASE

No actinometer absorbs every photon from 295 to 700 nm with the same absorbance and quantum efficiency. The most useful light for photodegradation of a chemical is generally in the range 295 - 450 nm (dyes excepted). The incident polychromatic light can be restricted to this range (a narrower range, if limited at 295 nm, can also be used). Few accurate actinometers, with high absorbance and constant quantum-yield in the range 295-450 nm, are available. The two most commonly used are based upon :

- photoreduction of potassium ferrioxalate
($\phi = 1.24$ at 302 nm, $\phi = 1.01$ at 436 nm)
- photoreduction of uranyl oxalate
($\phi = 0.57$ at 302 nm, $\phi = 0.58$ at 436 nm)

A full description of these two actinometers is given by Pitts et al (48). The quantum yield ϕ_a of oxidation-reduction in both these actinometers can be considered as constant between 295 and 450 nm.

The rate of formation of Fe^{2+} (in the ferrioxalate technique)* or the rate of decomposition of oxalic acid (in uranyloxalate) is

$$r = \phi_a \int_{295}^{450} I_a(\lambda) \cdot d\lambda$$

Where work at wavelengths longer than 450 nm is necessary, alternative means for measuring the incident light quantity (e.g. a thermophile) must be used.

The experimental determination of r affords the total number of incident photons (I_{ot}). The relative spectral energetic distribution of each source is given by the makers. The relative number of photons in each spectral range (for example of 20 nm width) is

* for better accuracy, in ferrioxalate

$$r = \int_{295}^{450} \phi_a(\lambda) \cdot I_a(\lambda) \cdot d\lambda$$

the fraction of these incident photons as in table 1 (given as an example; it must be adapted according to any particular source). In each spectral range, the absolute number of incident photons is :

$$I_{oi} = \alpha_i \cdot I_{ot}$$

TABLE 1

High pressure	Spectral range in nm	295/ 310	310/ 330	330/ 350	350/ 370	370/ 390	390/ 410	410/ 430	430/ 450	Σ
Xenon source	relative emitted energy	77.3	98.7	120.2	128.8	133	150	150	160	
	relative number of incident photons	2.32	3.16	4.09	4.64	5.05	6	6.30	7.05	38.61
	α_i	0.06	0.08	0.10 ₅	0.12	0.13	0.15 ₅	0.16	0.18	1
High pressure Mercury source	relative emitted energy	13	17	11	32	2	18	2	24	
	relative number of incident photons	3.9	5.3	3.7	11.7	0.8	7.2	0.8	10.6	44
	α_i	0.09	0.12	0.08	0.26	0.02	0.16	0.02	0.24	1

APPENDIX 9 : DETERMINATION OF QUANTUM YIELD (ϕ)

The experimental value of ϕ can be used in the computation of the lifetime if the following checks have been carried out :

- ϕ must be shown to be independent of the absorbed intensity
- ϕ must be shown to be independent of the initial concentration $[P]_0$. This last experiment can be performed at, $[P]_0 \cdot l = \text{constant}$,

a technique which avoids corrections of the absorbed intensity since the optical density $\epsilon \cdot [P]_0 \cdot l$ and absorbed intensity are kept constant. In any case, too high initial concentrations are irrelevant since a "skin effect" (absorption in the first layers) and self-quenching can occur.

Diffusion of oxygen in the liquid phase must not control the rate of the photochemical reaction. Saturation by oxygen must be ensured, by means of supersaturation for example. For most compounds, ϕ is independent of the absorbed intensity I_a and initial concentration $[P]_0$. If not, measurement of ϕ and computation of τ must be performed for the same values of I_a and $[P]_0$. In many cases, ϕ is pH dependent.

In a condensed phase the quantum yield does not depend upon the excitation wavelength λ provided that the same transition $S_0 \rightarrow S_x$ is occurring, i.e. in so far as photons are absorbed in the same electronic band. Excitation into upper states, $S_2, S_3, \dots$ leads to the same value of ϕ if internal conversions have unit efficiency, which might not always be the case. It is thus recommended to measure ϕ through excitation into the first electronic band $S_0 \rightarrow S_1$ (long wavelength side of absorption spectra). A check of the variations of ϕ with excitation into $S_2, \dots$ must be carried out with different filtered lights. For practical reasons, it is easier to cut off short wavelengths; $\phi(S_1)$ must be compared with $\phi(S_1 + S_2) \dots$ (again, the use of monochromatic light is easier). In aqueous solution, electronic bands are rather broad. For example in p-nitrophenol, the $S_0 \rightarrow S_1$ electronic band spreads from

270 nm to 400 nm for the molecular form (e.g. the pK of p-nitrophenol is close to 6.8).

If the 295-450 nm radiations are absorbed in the same electronic band (as in p-nitrophenol) no further filtration is needed. The rate of disappearance R of the photodegradable compound is measured experimentally and the quantum yield ϕ is computed as

$$\phi = \frac{R}{\int_{295}^{450} I_a(\lambda) \cdot d\lambda}$$

The total absorbed intensity $\int_{295}^{450} I_a(\lambda) \cdot d\lambda$ is computed simply

as a sum of photons absorbed in each spectral range. In a narrow range, the number of photons absorbed is related to the known number of incident photons (measured by actinometry) by the Beer-Lambert law:

$$I_a(\lambda) = \frac{1000}{\ell} I_{oi} (1 - 10^{-\epsilon [P_o] \cdot \ell})$$

where $[P_o]$ = initial concentration in M.

ℓ = the optical path in cm

ϵ = the mean molar extinction coefficient in each spectral range (known from the absorption spectrum). If ϵ is changing rapidly with wavelength, a narrower spectral width should be used (No computer is needed).

If the 295-450 nm radiations are absorbed in two electronic bands, specific excitation into the first excited state S_1 is needed through further filtration. The corresponding disappearance rate $R(S_o-S_1)$ and quantum yield $\phi(S_o-S_1)$ are determined.

$$\phi(S_o-S_1) = \frac{R(S_o-S_1)}{\int_{S_o-S_1} I_a(\lambda) \cdot d\lambda}$$

Then the overall disappearance rate R must be measured under the whole excitation (295-450 nm):

$$R = R(S_0-S_1) + R(S_0-S_2)$$

The quantum yield $\phi(S_0-S_2)$ is computed as :

$$\phi(S_0-S_2) = \frac{R(S_0-S_2)}{\int_{(S_0-S_2)} I_a(\lambda) \cdot d\lambda}$$

Sometimes $\phi(S_0-S_2)$ is different from $\phi(S_0-S_1)$.

APPENDIX 10 : PHOTODEGRADATION OF 4-NITROPHENOL IN WATER
DETERMINATION OF LIFETIME

The experimental steps include the following :

1. Recording of absorption spectra at different pH's
 (see graph);
 determination of $\epsilon(\lambda)$.
2. Measurement of quantum yield of disappearance of
 4-nitrophenol at different pH's : $\phi (S_0 - S_1)$.

These measurements have been carried out in mono-chromatic light.

pH	1.4	1.4	5 distilled water	11.5	11.5
(O ₂) dissolved	$3.10^{-4}M$	0	$3.10^{-4}M$	$3.10^{-4}M$	0
ϕ	$8.5 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	8.10^{-5}	7.10^{-6}	$1.2 \cdot 10^{-5}$

(pK 4-nitrophenol = 6.9)

3. Computation of the lifetime of 4-nitrophenol in
 environmental conditions - daylight - Chicago -
 noon - summertime.

i) I_0 at various wavelengths (λ) :

λ (nm)	290	310	330	350	370	390	410	430	450
I_0 ($\mu W/cm^2/nm$)	0	15	40	70	85	116	145	163	180

ii) The lifetime has to be calculated from

$$\tau = \frac{1}{2300 \int_{295}^{450} \phi(\lambda) \cdot \epsilon(\lambda) \cdot I(\lambda) \cdot d\lambda}$$

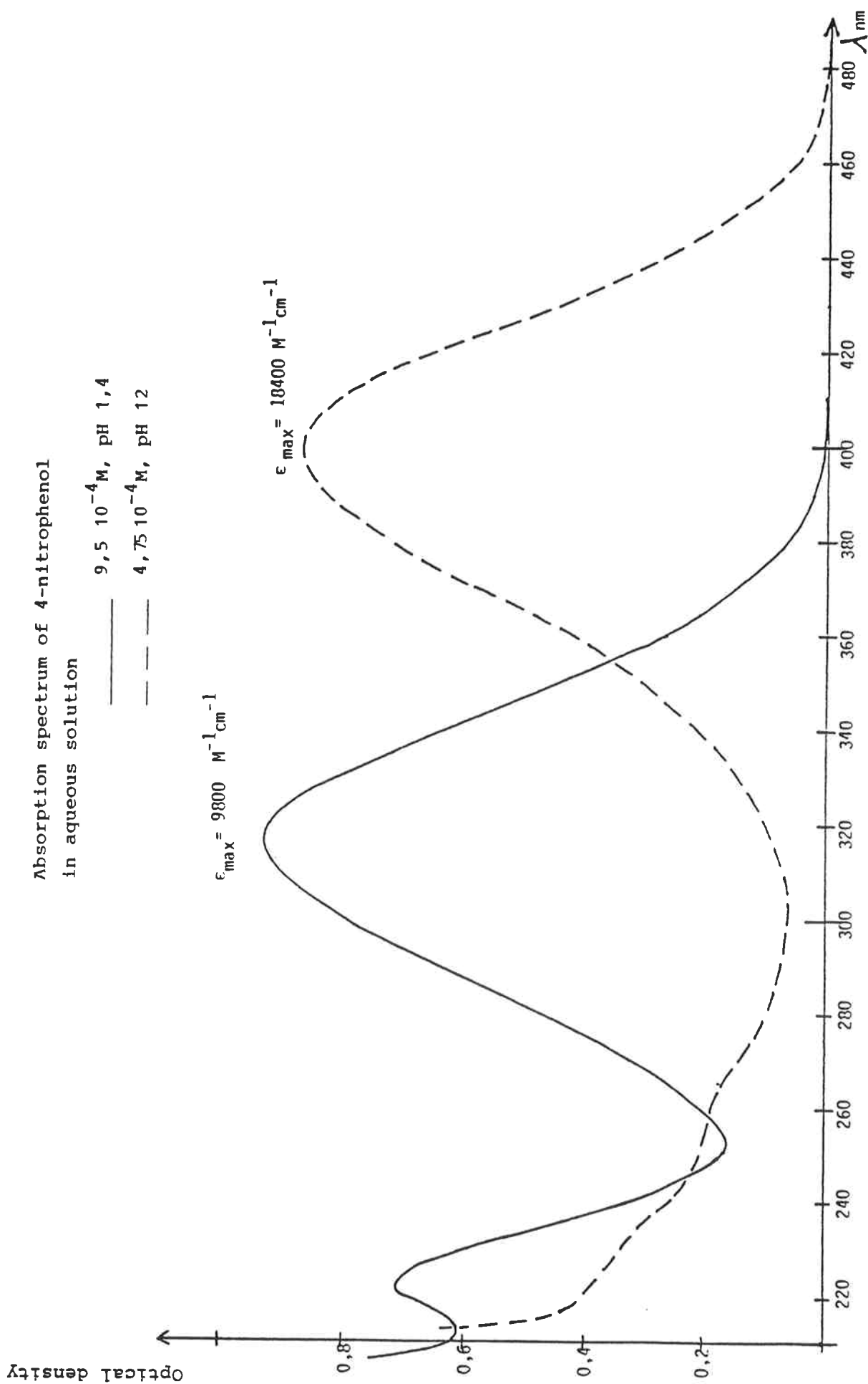
iii) Derivation of values of the integral in above equation for τ :

λ (nm)	$I_0 \times \Delta\lambda \times 10^{10}$ ($\text{cm}^{-2} \cdot \text{s}^{-1}$)	At pH 1.4 and 5.5		At pH= 11.5	
		$\epsilon \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-1}$	$\epsilon \times I_0 \Delta\lambda \times 10^6$	$\epsilon \times 10^{-4}$ ($\text{M}^{-1} \text{cm}^{-1}$)	$\epsilon \times I_0 \Delta\lambda \times 10^6$
300	1.88	0.847	1.59	0.120	0.226
320	14.7	0.963	14.16	0.200	2.94
340	31.3	0.663	20.75	0.446	13.96
360	46.7	0.284	13.26	0.916	42.78
380	63.9	0.068	4.35	1.547	98.85
400	87.3	0.008	0.70	1.836	160.28
420	108.2	0.000	0.00	1.337	144.66
440	126.2	0.000	0.00	0.558	70.42
		$\Sigma = 54.8$		$\Sigma = 534.1$	

iv) Final calculation of lifetime (τ) :

pH= 1.4	$\int_{300}^{440} \epsilon I_0 10^6 d\lambda = 54.8$	$\phi = 8.5 \times 10^{-5}$	$\tau = \frac{10^6}{2300 \times 8.5 \times 10^{-5} \times 54.8} = 10^5 \text{ s}$ $= 26 \text{ h}$
pH= 5.5	$\int_{300}^{440} \epsilon I_0 10^6 d\lambda = 54.8$	$\phi = 8 \times 10^{-5}$	$\tau = \frac{10^6}{2300 \times 8 \times 10^{-5} \times 54.8}$ $= 27,5 \text{ h}$
pH = 11.5	$\int_{300}^{440} \epsilon I_0 10^6 d\lambda = 534.1$	$\phi = 7 \times 10^{-6}$	$\tau = \frac{10^6}{2300 \times 7 \times 10^{-6} \times 534.1} = 1.16 \times 10^5 \text{ s}$ $= 32,3 \text{ h}$

The pH effect is attenuated by the shift of the absorption spectrum.



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