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

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## A. SUMMARY

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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, O<sub>3</sub>, 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 OH· 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 OH· 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

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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<sup>\*</sup> 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<sup>\*</sup> 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,  $\text{NO}_x$ , air and light alone comprises more than 200 reactions (8). According to the present state of our knowledge there are essentially two species, the  $\text{OH}^{\cdot}$  radical and ozone, which cause the degradation of an organic compound in the atmosphere by oxidation.