

Executive Summary of Photolysis Studies

3M has completed a series of studies of the direct and indirect photolytic reactions of four materials; Table 1 lists the materials, their chemical abbreviations, and the relevant 3M report numbers. The purpose of the studies was to provide information regarding the photolytic stability of these materials under environmentally relevant conditions. The materials were specific (monomeric) compounds potentially related to the manufacture and/or environmental persistence of the more complex materials.

Three of these studies are based on samples in aqueous solutions. The analytical methods developed by 3M for these studies are ETS-9-46.0, ETS-9-44.0, ETS-9-49.0, ETS-8-177.0, ETS-8-176.0, ETS-8-182.0, and ETS-8-181.0. The methods are based on OPPTS: 835.5270 and the OECD Draft Document "Phototransformation of Chemicals in Water - Direct and Indirect Photolysis" (August 2000). The studies are GLP-like; many GLP standards were used in the studies, and the quality assurance procedures followed were based on the practices described in the GLP documentation (40 CFR Part 792, TSCA).

The three aqueous studies included the preparation of replicate samples of each material at 25°C under several radical precursor conditions. After incubation under UV irradiation and over specific time periods, samples were analyzed by HPLC/MS and/or GC/MS to provide quantitative information on the test compounds and potential degradation products.

First-order kinetic theory provides a suitable framework for interpretation of all the analytical results; Table 2 lists the results of these interpretations.

No evidence of direct photolysis was noted in any of the studies.

In the indirect photolysis studies of PFOS and PFOA, no degradation products were observed. However, using data obtained for the iron-rich matrix (with and without added H₂O₂), an estimated minimum indirect photolytic half-life was calculated.

Indirect photolytic degradation of *N*-EtFOSE alcohol was observed in each test matrix, but the observed rates and product distribution varied from matrix to matrix. The three primary degradation products observed were PFOA, *N*-EtFOSA, and FOSA; however, under certain conditions, trace levels (near the quantitation limits) of other potential degradation products (heptadecafluorooctanes and PFOS) were also observed. It remains unclear whether these compounds were produced by the degradation of *N*-EtFOSE alcohol or by degradation of low-level impurities in the original test material.

One study (that of POSF) employed gas phase samples prepared at 33°C. In these studies, an ultraviolet lamp irradiated various sample and control mixtures of POSF, CH₃Cl (a reference compound), ozone and water vapor in a reaction chamber. FTIR spectroscopy provided in-situ measurements of the reactant concentrations under various sample and control conditions. The POSF study showed degradation in only one of seven runs. Data

from that run, in conjunction with published values of the tropospheric OH radical concentration and related reaction rates for CH₃Cl, provides an estimate of the minimum POSF half-life due to reactions between POSF and the OH radical.

Table 1. Information Regarding Compounds Involved in Indirect Photolysis Studies		
Compound	Abbreviation	3M Report Number and Date
Perfluorooctanesulfonate - potassium salt	PFOS	W2775 (April 23, 2001)
2-(<i>N</i> -Ethylperfluorooctanesulfonamido)-ethyl alcohol	<i>N</i> -EtFOSE alcohol	W2783 (April 19, 2001)
Perfluorooctanoic acid - ammonium salt	PFOA	E00-2192 (April 20, 2001)
Perfluorooctanesulfonyl fluoride	POSF	E01-0739 (June 12, 2001)

Table 2. Summary of Indirect Photolysis Study Results			
Compound Abbreviation	Matrices Studied	Max. Photolysis Period (hours)	Estimated Half-Life at 25°C
PFOS	Aqueous: H ₂ O (pH 7) Iron oxide/H ₂ O ₂ Synthetic Humic	167	≥ 3.7 years*
<i>N</i> -EtFOSE alcohol	Aqueous: H ₂ O (pH 7) Iron oxide/H ₂ O ₂ Synthetic Humic H ₂ O ₂ -rich	72	40 days
PFOA	Aqueous: H ₂ O (pH 7) Iron oxide/H ₂ O ₂ Synthetic Humic	164	≥ 349 days*
POSF	Gaseous: O ₃ , H ₂ O, CH ₃ Cl in the presence of UV radiation	N/A	≥ 3.7 years*

*No loss of parent analyte quantified. The ≥ result is based on measurement uncertainties.