Study Title

Screening Studies on the Aqueous Photolytic Degradation of 2-(*N*-Ethylperfluoroctanesulfonamido)-ethyl alcohol (N-EtFOSE Alcohol)

Data Requirement

Consistent With:

OPPTS: 835.5270 "Indirect Photolysis Screening Test"

-and-

OECD Draft Document "Phototransformation of Chemicals in Water - Direct and Indirect Photolysis", August 2000

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Study Completion Date

April 19th, 2001

Performing Laboratory

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Project Identification

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Compliance Statement

Study Title: Screening Studies on the Aqueous Photolytic Degradation of 2-(*N*-Ethylperfluorooctanesulfonamido)-ethyl alcohol (N-EtFOSE Alcohol)

Study Identification Number: W2783

This study was not designed to be performed in accordance with the GLPs. Thus, it does not comply with the requirements of the US EPA Good Laboratory Practices Standards at 40 CFR Part 792 (TSCA). However, all raw data and the final report have been audited.

Test and reference substance receipt and use, dosing and incubation of the test system, and analyses were conducted and documented according to procedures developed by 3M, based upon on OPPTS: 835.5270 "Indirect Photolysis Screening Test" and OECD Draft Document "Phototransformation of Chemicals in Water - Direct and Indirect Photolysis", August 2000, and documented according to GLP procedures. All raw data and the final report are maintained in the 3M Environmental Laboratory archives.

Study Director — Date 04/24/01

Sponsor Representative — Date 04/24/01

Quality Assurance Statement

Study Title: Screening Studies on the Aqueous Photolytic Degradation of *N*-(Ethylperfluoro-octanesulfonamido)-ethyl alcohol (N-EtFOSE Alcohol)

Study Identification Number: W2783

This study has been inspected by the 3M Laboratory Quality Assurance Unit as indicated in the following table. The findings were reported to the study director and laboratory management.

Inspection Dates	Phase	Date Reported to	
		Management	Study Director
03/30/01-04/05/01	Data	04/06/01	04/06/01
03/30/01-04/05/01	Draft Report	04/16/01	04/16/01

Ken Litt — 4/20/01

Quality Assurance Unit — Date

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Location of Archives

Digital copies of original data, and all original paper data have been archived and will be retained in the 3M Environmental Laboratory archives for at least 10 years.

Summary

We report here the results of studies to determine the aqueous photolytic stability of 2-(*N*-ethylperfluorooctanesulfonamido)-ethyl alcohol (N-EtFOSE alcohol) and to identify the primary degradation products. Our techniques are based on both EPA and OECD guidance documents.[9,10] In this study, both direct photolysis (the interaction of light with the target molecule leading to a chemical change) and indirect photolysis (the interaction of light with the sample matrix to produce radical species that subsequently react with the target material) were studied using a synthetic light source.

The primary findings established that the rate of photodegradation by direct photolysis is negligible and the primary products of indirect photolysis are perfluorooctanoic acid, *N*-ethylperfluorooctane sulfonamide and perfluorooctane sulfonamide. Rates of indirect photolytic degradation are highly dependent on experimental conditions however, using an iron oxide (Fe_2O_3) photoinitiator matrix model an environmental half-life estimate of 40 days was determined.

Introduction

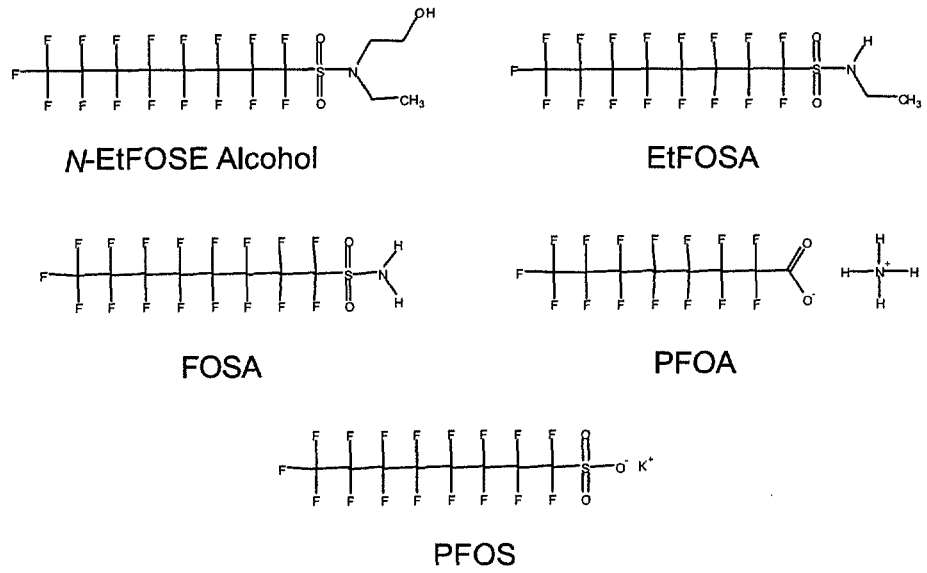
Photolysis reactions are primary routes of degradation of chemical compounds in the environment (hydrolysis and biodegradation are two others). A study of photo-induced reactions will yield information on the persistence of the parent material and information on the identity and stability of products formed. Photolytic reactions occur by two types of mechanisms. The first mechanism, direct photolysis, can be defined as the direct absorption of a photon by the target species that leads to a chemical change. The second mechanism, indirect photolysis, can be loosely defined as a chemical or electronic excitation transfer from a light absorbing species to the test substance which then undergoes some type of chemical change. In the present investigation, photons from a light source were used to either induce a direct chemical change in N-EtFOSE alcohol or to induce the formation of radicals from the sample matrix, which then produced a chemical change in the test substance.

The test material, N-EtFOSE alcohol was dissolved in an aqueous solution that was exposed to simulated sunlight to test for direct photolysis.[1,2] To test for indirect photolysis, *N*-EtFOSE alcohol in four separate aqueous photoinitiator matrices were exposed to simulated sunlight for periods of time from 69.5 to 72 hours. These exposures tested how each particular matrix affected both the overall rate of decomposition as well as the observed product distribution. The first test matrix was an aqueous solution to which H_2O_2 was added as a well characterized source of •OH radicals.[3,4] This was used to test for the propensity of N-EtFOSE alcohol for indirect photolytic decomposition. The second matrix contained a dilute aqueous $CaCl_2$ solution and a well-characterized soil. This matrix was used to test the effects that adsorption-desorption equilibria, surface induced reactions and "•OH quenching"[5] could have on indirect photolytic decomposition. The third matrix contained Fe_2O_3 in water, as this matrix has been shown to generate hydroxyl radicals via a Fenton-type reaction in the presence of both natural and artificial sunlight.[6,7] The fourth matrix was a standard humic material[8] and was consistent with a modified procedure based on the US EPA methodology, OPPTS 835.5270 "Indirect Photolysis Screening Test"[9] as well as OECD Draft Document "Phototransformation of Chemicals in Water - Direct and Indirect Photolysis", August 2000[10].

To effectively determine photolytic decomposition, the concentration of parent material must be monitored over time. While this will determine the rate, it is also important to understand what the degradation products are and how much of each are formed. The present investigation quantified the parent material and the four predicted degradation products by LC/MS as shown in Figure 1 were EtFOSA is *N*-ethylperfluorooctanesulfonamide, PFOA is ammonium-perfluorooctanoic acid, FOSA is perlfluorooctanesulfonamide and PFOS is potassium-perfluorooctanesulfonate.

Because of the possibility of volatile degradation products, it was decided to monitor for selected C_2 through C_8 2- or 3- substituted perfluoronated olefins (e.g. C_8F_{16}) and 1- or 2-substituted hydrides (e.g. $C_8F_{17}H$) in the iron-rich matrix by dynamic purge and trap gas chromatography/mass spectrometry.

Figure 1. Structures of the Compounds Observed by LC/MS Analysis



Determination of the kinetic rate constant (k_p) was based only upon the data from the iron rich matrix using the following equation under the assumption that the kinetics was first order. (See Appendix C for complete kinetic derivations and exact mathematics for half-life calculations.)

$$k_P t = -\ln\left(\frac{P}{P_0}\right) \qquad \text{(C8)}$$

Where t represents elapsed time, P represents the measured concentration of the parent after exposure and P_0 represents the initial concentration.

The half-life of N-EtFOSE alcohol ($T^{1/2}_p$) is related to the determined rate constant by the following equation.

$$T^{1/2}_p = \frac{\ln(2)}{k_P} \qquad \text{(C9)}$$

Materials and Methods

Chemical Characterization

Information on the chemical characterization of both reference substances and control substances is presented in Appendix B.

Method Summaries

Copies of all analytical methods used in this investigation are attached in Appendix A "Analytical Methods". Equipment settings, conditions and complete quality control parameters are listed within those specific methods.

UV/Visible analysis were performed following 3M Environmental Laboratory Method **ETS-9-46.0** "Operation and Maintenance of the Hewlett Packard 8453 UV-Visible Spectrophotometer" An aqueous saturated solution of N-EtFOSE alcohol was prepared and an initial UV/VIS spectrum recorded. Absorbance over the range 190-1100 nm was recorded. No absorbance over baseline was detected.

Sample preparation for this analysis followed 3M Environmental Laboratory Method **ETS-8-177.0** "Indirect Photolysis Screening Tests in Synthetic Humic Water" or **ETS-8-176.0** "Preparation of Samples for Photolytic Exposure Studies in Aqueous Matrices". A typical sample preparation table for an indirect photolysis screening test is shown in table 1 on the following page.

The general method of sample preparation is as follows. For each time point under each condition shown in table 1, ten 40-mL sample screw cap VOA vials were prepared: sample, duplicate, triplicate, sample spike, matrix blank, matrix blank spike (assured no accidental contamination of matrix by target compounds), direct photolysis sample, direct photolysis sample spike (assured that degradation observed was due to indirect photolysis and not another process), control blank and control blank spike (assured no accidental contamination of the blank had occurred). All vials contained 5 mL of appropriate matrix: water, soil in water at 0.70XX g in 5 mL, Fe^{+3} at a 24X molar excess in water, and H_2O_2 was at 1:1 molar equivalent, added every 24 hours. Aliquots of N-EtFOSE alcohol were added to the vials as indicated in table 1. The initial time point vials (labeled as "Time Zero" on the sample preparation sheets in Appendix B) were then refrigerated at 4±2°C. These samples served as controls with which to determine what change, if any, occurred during the time the remaining vials were in the photoreactor. Exposed samples were placed upside down in a custom built holder in the photo-reactor. Unexposed samples were wrapped in aluminum foil, sealed in a plastic bag and placed under the sample rack inside the photo-reactor (these samples assured that any degradation or difference in degradation was due to photolysis and not some other process). During the course of the exposure, a water bath held the temperature of the water surrounding the bottom of the vials (which contained the aqueous samples) at 25 ± 3°C. The temperature of the chamber itself was allowed to drift to 70 ±10°C. When required, the H_2O_2 was added at each 24-hour interval by gas-tight syringe, through the VOA septa during the exposure period. After exposure, the samples were removed for analysis.

Selected portions of the sample setup were modified to accommodate additional samples, controls etc. to improve the quality control of the analysis or were modified in other ways out of experimental necessity. Details of these modifications are shown on the sample preparation sheets and the individual sample data sheets shown in Appendix D. For example, the sample setup for the soil rich matrix used quartz tubes (in quadruplicate rather than triplicate) as opposed to VOA vials. The portion of the study that used iron oxide as a radical generating species was set up with triplicate samples and duplicate sample spikes while the aqueous study was set up using duplicate samples rather than triplicate due to space limitations.

The artificial light source used in this analysis was either a Suntest CPS+ or Suntest XLS+, the operation of which followed 3M Environmental Laboratory Method **ETS-9-44.0** "Operation and Maintenance of the Sunlight Exposure System, Immersion Unit, and Recirculating Water Chiller System". The output of light from this equipment was set at the desired intensity and held constant by a continuos internal feed back loop between an internal radiometer and the variable light source. Intensity was set at 680 w/m^2.

Table 1. Typical Sample Preparation Scheme Used in the Present Investigation

						LC/MS*		GC/MS*	
Description	Test Matrix	Control Matrix	Test Substance	Post Photolysis Target Analyte spike	Sample Type	With H_2O_2	W/out H_2O_2	With H_2O_2	W/out H_2O_2
Ind. Photo. Sample Rep 1	+	0	+	0	Initial Time Point	X	X	X	X
Ind. Photo. Sample Rep 2	+	0	+	0	Initial Time Point	X	X	X	X
Ind. Photo. Sample Rep 3	+	0	+	0	Initial Time Point	X	X	X	X
Ind. Photo. Sample Spike	+	0	+	+	Initial Time Point	X	X	X	X
Matrix Blank	+	0	0	0	Initial Time Point	X	X	X	X
Matrix Blank Spike	+	0	0	+	Initial Time Point	X	X	X	X
Direct Photo. Sample	0	+	+	0	Initial Time Point	X	X	X	X
Direct Photo. Spike	0	+	+	+	Initial Time Point	X	X	X	X
Control Blank	0	+	0	0	Initial Time Point	X	X	X	X
Control Blank Spike	0	+	0	+	Initial Time Point	X	X	X	X
Ind. Photo. Sample Rep 1	+	0	+	0	Exposed to Light	X	X	X	X
Ind. Photo. Sample Rep 2	+	0	+	0	Exposed to Light	X	X	X	X
Ind. Photo. Sample Rep 3	+	0	+	0	Exposed to Light	X	X	X	X
Ind. Photo. Sample Spike	+	0	+	+	Exposed to Light	X	X	X	X
Matrix Blank	+	0	0	0	Exposed to Light	X	X	X	X
Matrix Blank Spike	+	0	0	+	Exposed to Light	X	X	X	X
Direct Photo. Sample	0	+	+	0	Exposed to Light	X	X	X	X
Direct Photo. Spike	0	+	+	+	Exposed to Light	X	X	X	X
Control Blank	0	+	0	0	Exposed to Light	X	X	X	X
Control Blank Spike	0	+	0	+	Exposed to Light	X	X	X	X
Ind. Photo. Sample Rep 1	+	0	+	0	Not Exp. to Light	X	X	X	X
Ind. Photo. Sample Rep 2	+	0	+	0	Not Exp. to Light	X	X	X	X
Ind. Photo. Sample Rep 3	+	0	+	0	Not Exp. to Light	X	X	X	X
Ind. Photo. Sample Spike	+	0	+	+	Not Exp. to Light	X	X	X	X
Matrix Blank	+	0	0	0	Not Exp. to Light	X	X	X	X
Matrix Blank Spike	+	0	0	+	Not Exp. to Light	X	X	X	X
Direct Photo. Sample	0	+	+	0	Not Exp. to Light	X	X	X	X
Direct Photo. Spike	0	+	+	+	Not Exp. to Light	X	X	X	X
Control Blank	0	+	0	0	Not Exp. to Light	X	X	X	X
Control Blank Spike	0	+	0	+	Not Exp. to Light	X	X	X	X

+ = added to test vial; 0 = NOT added to test vial; *Duplicate sets, one with H_2O_2, one without (excludes the Humic material test where H_2O_2 was not added)

GC/MS analysis followed 3M Environmental Laboratory Method **ETS-8-182.0** "Analysis of Fluorochemicals by Archon Purge and Trap Autosampler, Tekmar Purge and Trap Concentrator and Agilent Gas Chromatograph/Mass Spectrometer". Equipment settings, separation conditions and ions monitored are present in this method. Equipment procedures for the GC/MS system followed 3M Environmental Laboratory SOP **ETS-9-49.0** "Routine Maintenance of Archon Purge and Trap Autosampler, Tekmar Purge and Trap Concentrator and Agilent Gas Chromatograph/Mass Spectrometer".

The HPLC/MS analysis followed 3M Environmental Laboratory Method **ETS-8-181.0** "Analysis of Photolysis Samples for Fluorochemicals by High Performance Liquid Chromatography With Mass Spectrometry Detection". Equipment settings, separation conditions and ions monitored are present in this method.

Study Deviations

Gas chromatography/mass spectrometry (GC/MS) was used for the analysis of volatile degradation products in the indirect photolysis test, the Fe^{+3} matrix and the H_2O_2 rich matrix. GC/MS analysis of the humic material matrix and the soil rich matrix were not performed. During the time course of that portion of the investigation, the instrumentation was unavailable.

The LC/MS analysis of the samples from the soil containing matrices showed low levels of background PFOS contamination. The sample preparation sheets that contained the soil weights (0.70XX grams, where X is unknown) were misplaced. Further, the control samples, or those without soil, showed poorer than expected mass balance. Due to these three factors, the data should be treated as semi-quantitative. If more definitive information is desired, additional studies are recommended.

The matrix containing the synthetic humic material showed unexpectedly slow photolytic decomposition of N-EtFOSE alcohol. This may have been due to excessive bleaching of the material. A second possible problem was that while setting up additional experiments in this matrix, the commercial humic material (Aldrich) was determined to contain the approximately 1 ppm dissolved organic carbon when the solution was prepared as recommend in reference 9 rather than the specified 6 ppm. The study director believes that the second explanation is the most probable and that the reaction was slower due to the lack of available radical generating species. Specific samples that failed data quality objectives are shown in Appendix D.

Results and Discussion

Data Quality Objectives

The following data quality objectives are from the method used in the present study.

- **Calibration curves.** An acceptable coefficient of determination (R^2) for linear curves is 0.990 or greater. Curve linearity, intercept, and quantitation accuracy should be verified, particularly at upper and lower calibration limits. Residuals generated in curve-fitting must be within ± 25% of true value. Alternative methods of curve-fitting (e.g., quadratic) require a correlation coefficient (r) of 0.990 or greater. Record the reason(s) for using quadratic curve-fitting, in the raw data.
- **Solvent blanks, Matrix blanks, Control blanks.** Blanks should show no more than 5% of the level of a high standard or CCV and should show less than 25% of the lowest point of the calibration curve. If solvent blanks show more than a 5% carryover, it may be necessary to rule out instrument contamination using duplicate solvent blank injections. If, after duplicate solvent blanks, there is still more than 5% carry-over, or the LOQ is adversely affected, the run should be stopped. This indicates that the instrument is contaminated and should be thoroughly cleaned.
- **Sample spikes, Matrix spikes, Control spikes.** Acceptable spike recoveries are greater than 75% or less than 125%. Values outside this range must be documented and evaluated by the Team Leader or designated supervisor.
- **Sample duplicates, triplicates or quadruplicates.** All samples are prepared with multiple replicates. Acceptable deviation or RSD precision values are less than or equal to 25%. Values above 25% must be documented and evaluated by the Team Leader or designated supervisor.
- **Continuing calibration verification (CCV).** Analyte concentration must not vary by more than ±25% of its expected value, relative to the initial calibration curve. Accept only those samples analyzed before the most recently accepted calibration verification. Reanalyze remaining samples with a new calibration curve.
- **Limit of Quantitation.** The limit of quantitation (LOQ) is equal to the lowest standard in the calibration curve that has an area greater than or equal to four times the solvent blanks and shows a residual less than 25% of the actual value.
- **Control Samples.** Control samples were required to be within ±25% of the nominal concentration.

Analytical Results

Data quality objectives for this study, outlined in the 3M laboratory method for this study (see Appendix A), were met, with the exceptions noted in the Deviations section.

- **Calibration curves.** Calibration curves were prepared according to the particular target at the required levels. For example, calibration curves for N-EtFOSE alcohol typically ranged from 25 to 1000 ppb. Calibration curves for degradation products for analysis by LC/MS typically ranged from 5-200 ppb. Calibration curves for GC/MS analysis of degradation products ranged from 1 ppb to 20 ppb. Using these standards, calibration curves were run

before and after every analytical sequence. A correlation coefficient (r) of 0.990 or greater was achieved for all curves.

- **Solvent blanks.** All solvent blanks (MeOH) were less than 25% of the method LOQ. In certain cases, as noted in the Deviations section, the LOQ was raised so that the solvent blanks met this criteria.
- **Sample spikes.** All spike recoveries were between 75 and 125%, except where noted in Appendix D.
- **Sample duplicates, triplicates or quadruplicates.** All sample RSD values were 25% or less except those noted in Appendix D.
- **Continuing calibration verification.** All CCV samples were within 25% of the expected value.
- **Method Blanks.** All method blanks were below 25% of the LOQ except those from the soil rich matrix (see deviations section for discussion).
- **Control Samples.** All control samples were within 25% except were noted in Appendix D.
- **Limit of Quantitation.** The LOQ varied dependant upon target. In some cases, the LOQ was adjusted to a higher level to meet criteria by deleting the lowest standard. In certain instances, numbers are reported below LOQ. This was allowed when the compound was clearly present in the sample. The numbers are tagged and labeled as being below LOQ.

Data Summary and Discussion

Direct and indirect photolytic decomposition of N-EtFOSE alcohol was tested in four separate matrices. These matrices were exposed to 680 w/m^2 of light over the wavelength range of 290-800 nm for time periods of 69.5-72 hours. Products observed and mass balance determinations for synthetic humic water, hydrogen peroxide in water and iron oxide containing water are shown in table 2.

The purity of N-EtFOSE alcohol was 97.8%, thus 2.2% of the material by weight was unknown. In portions of the indirect photolysis experiments, volatile materials, mainly $C_8F_{17}H$, were detected at levels less than 0.25% by mass. Thus, it is difficult to determine if these materials were the result of degradation of the parent material or the impurities. As is the case with the volatiles, PFOS was detected in certain portions of the study at levels less than 0.4% by mass. Again, it is difficult to ascribe the appearance of the material to degradation of the parent or the impurity.

Direct photolytic decomposition of N-EtFOSE alcohol could not be determined as two separate exposures gave two different results. The data from table 2a "direct photolysis sample" showed levels of N-EtFOSE alcohol within experimental error both before and after exposure. At the same time, the appearance of low levels of EtFOSA representing 0.54% by mass of the original mass of N-EtFOSE alcohol was detected. However, data from table 2c (water only) showed a similar trend for N-EtFOSE alcohol and no appearance of any degradation product. Because the N-EtFOSE alcohol used in this study was 97.8% pure, the appearance of the low levels of EtFOSA may represent degradation of an unknown impurity rather than degradation of the parent material. However, it can be stated that direct photolytic decomposition of N-EtFOSE alcohol (or impurities) is a very slow reaction. The UV/Vis spectrum of the test material showed

no measurable absorbance but is also inconclusive in supporting direct photolysis due to the low solubility of N-EtFOSE alcohol (~150 ppbv) in water.

Table 2. Observed Products and Mass Balance Determinations for Direct and Indirect Photolysis in Water, Iron Oxide Containing Water and Synthetic Humic Water

2a. Matrix: Water, With and Without H_2O_2

Time of exposure was 69.5 hours		EtFOSE-OH	PFOA	PFOS	FOSA	EtFOSA	Volatiles	Mass Balance
Sample	Condition	nMoles	nMoles	nMoles	nMoles	nMoles	nMoles	(percent)
Ind. Photo. Sample[1]	Initial Time Point	93.86	ND	ND	ND	0.37	ND	104%
Dir. Photo. Sample[2]	Initial Time Point	94.19	ND	ND	ND	ND	ND	104%
Ind. Photo. Sample[1]	Exposed to Light	57.39	5.53	ND	0.53	3.33	0.075	74%
Dir. Photo. Sample[2]	Exposed to Light	77.71	ND	ND	ND	0.49	ND	87%
Ind. Photo. Sample[1]	Not Exposed to Light	63.03	4.09	ND	0.48	3.36	ND	78%
Dir. Photo. Sample[2]	Not Exposed to Light	91.62	ND	ND	ND	ND	ND	101%
Detection Limits		1.59	0.24	0.20	0.21	0.2	0.0095*	

Vials initially contained 90.35 nMoles N-EtFOSE alcohol. 1. Indirect Photloysis Sample: These samples had H_2O_2 added (1:1 molar equivalance) as a radical source every 24 hours they were in the reactor, results are from duplicate samples. 2. Direct Photolysis Sample: These samples did not have H_2O_2 added, results are from duplicate samples. *Sum total of all volatiles. ND = non detect.

2b. Matrix: Fe_2O_3 in Water, With and Without H_2O_2

Time of exposure was 69.5 hours		EtFOSE-OH	PFOA	PFOS	FOSA	EtFOSA	Volatiles	Mass Balance
Sample	Condition	nMoles	nMoles	nMoles	nMoles	nMoles	nMoles	(percent)
Fe_2O_3 W/H_2O_2[1]	Initial Time Point	79.30	2.64	ND	ND	3.27	ND	94%
Fe_2O_3 WO/H_2O_2[2]	Initial Time Point	93.61	ND	ND	ND	ND	ND	104%
Fe_2O_3 W/H_2O_2[1]	Exposed to Light	ND	41.35	0.41	20.98	0.36	0.14	70%
Fe_2O_3 WO/H_2O_2[2]	Exposed to Light	59.53	7.54	0.33	0.39	4.33	ND	80%
Fe_2O_3 W/H_2O_2[1]	Not Exposed to Light	61.34	5.36	ND	0.87	4.20	ND	79%
Fe_2O_3 WO/H_2O_2[2]	Not Exposed to Light	90.01	ND	ND	ND	0.23	ND	100%
Detection Limits		1.59	0.24	0.20	0.21	0.2	0.0095*	

Vials initially contained 90.35 nMoles N-EtFOSE alcohol. 1. Samples had H_2O_2 (1:1 molar equivalance) as a radical source every 24 hours and Fe_2O_3 added (24 Fe^{+3}:1 N-EtFOSE-OH molar equivalance) as a radical generating species, results are from quadripulate samples. 2. Samples contained just Fe_2O_3 (24 Fe^{+3}:1 N-EtFOSE-OH molar equivalance) as a radical generating species, results are from quadripulate samples. *Sum total of all volatiles. ND = non detect.

2c. Matrix: Synthetic Humic Water

Time of exposure was 72.0 hours		EtFOSE-OH	PFOA	PFOS	FOSA	EtFOSA	Mass Balance
Sample	Conditions	nMoles	nMoles	nMoles	nMoles	nMoles	(percent)
Humic Water[1]	Initial Time Point	7.55	ND	ND	ND	ND	111%
18.2 MΩ Water[2]	Initial Time Point	7.40	ND	ND	ND	ND	109%
Humic Water[1]	Exposed to Light	6.51	0.25	ND	ND	ND	99%
18.2 MΩ Water[2]	Exposed to Light	6.39	ND	ND	ND	ND	94%
Humic Water[1]	Not Exposed to Light	7.39	ND	ND	ND	ND	109%
18.2 MΩ Water[2]	Not Exposed to Light	7.52	ND	ND	ND	ND	111%
Detection Limits		0.17	0.20	0.16	0.18	0.17	

Vials initially contained 6.80 nMoles N-EtFOSE alcohol. 1. Samples contained Humic Materials, samples are from triplicate analysis. 2. Samples were plain water, results are from duplicate samples. ND = non detect.

As was noted in the introductory section, the addition of hydrogen peroxide to water was done to determine the propensity of N-EtFOSE alcohol to undergo indirect photolytic reactions with the hydroxyl radical. The results from table 2a show that N-EtFOSE alcohol will react with •OH radicals to form new products and establishes what the products are: PFOA, EtFOSA and FOSA. However, those samples that were not exposed to light showed a very similar loss of parent and distribution of products. It is believed that the loss of N-EtFOSE alcohol in the dark control samples that also contained H_2O_2 was due to the equilibrium reaction between H_2O_2 and the hydroxyl radical, the end result of which was decomposition of the parent material.

Indirect photolysis in the synthetic humic material was observed as forming PFOA (3.7% by mass PFOA formation) from the data in table 2c. As noted in the deviations section of this report, this matrix, when mixed according to prescribed procedures, did not contain the appropriate amount of dissolved organic carbon. Thus, the conclusion from this test is simply that indirect photolysis of N-EtFOSE alcohol does occur in matrices that contain humic materials but at an undetermined rate.

As observed in table 2b, the reaction between iron oxide, hydrogen peroxide and light with *N*-EtFOSE alcohol resulted in complete loss of the alcohol (Fe_2O_3 with H_2O_2 data). As with the reaction between *N*-EtFOSE alcohol and H_2O_2, the degradation products PFOA, FOSA and EtFOSA were observed and accounted for a sum total of 69.4% of the starting material by mass. However, trace levels of two new degradation products were observed: PFOS and volatiles. Because these two materials represent a combined total of only 0.61% of the original starting material, it is undetermined if these materials were degradation products from *N*-EtFOSE alcohol or degradation products from the impurities.

The reaction between light, Fe_2O_3 and *N*-EtFOSE alcohol is perhaps the most environmentally relevant reaction of those shown in table 2. The products of this reaction were PFOA, EtFOSA, PFOS and FOSA. As with that portion of the test utilizing H_2O_2, only a small amount of PFOS was observed (0.36% by mass) and it is difficult to establish if this is from the parent material or low levels of impurities. Because Fe^{+3} is ubiquitous in the environment, this test has direct relevance as an environmental model. Solving for the half-life (as shown in Appendix C), yielded an environmental half-life of 40 days at 45° south latitude in clear water and a cloudless sky. Based on the above results, the degradation pathway shown in figure 2 is proposed.

Preliminary 3M data has shown that N-EtFOSE alcohol has a high soil adsorption coefficient. To test for the effect that adsorption/desorption equilibria might have as well as possible surface induced photolytic reactions and possible hydroxyl radical quenching, N-EtFOSE alcohol was studied in the presence of three soil types. The first was an EPA synthetic soil mix representing a sandy clay loam, the second was a soil from Morgan County AL (USA) representing a soil with a high clay content and the third was a soil from St. Croix County WI (USA) representing a loam. Characterization data for these soils is shown in appendix F. Soil equilibration followed OECD method 106 "Adsorption - Desorption Using a Batch Equilibrium Method.[11] The results of this study are shown on the following page in table 3.

From the data in table 3 it is apparent that the soil-light combination can induce indirect photolytic decomposition of N-EtFOSE alcohol, both in the presence and absence of added H_2O_2. The data shows that the addition of H_2O_2 speeds up the reaction when compared to those samples without H_2O_2. When the data is compared against that from the direct photolytic test (Table 2a and c), it is concluded that something in the soil acts as a radical source for the

indirect photolytic decomposition of N-EtFOSE alcohol. The data from the three sample sets in table 3 which all contained H_2O_2 supports the hypothesis that soils will slow the reaction, probably by some type of •OH quenching. Because the soil itself can act to promote indirect photolysis, the role of adsorption-desorption equilibria remains unclear. As seen in table 3, the initial time point data and the data from those samples that were not exposed to light all showed levels of EtFOSA near the quantitation limit and represented less than 1% of the total EtFOSE concentration. This could be expected, as the starting material was only 97.8% pure. The compound PFOS was detected in all samples and controls of the Morgan County soil and probably reflects soil contamination rather than a chemical production. All indirect photolysis soil samples showed PFOS at low levels that were just above the quantitation limit. PFOS was also detected in all samples that were exposed to light that contained both soil and H_2O_2. Because of these low levels and detection of PFOS in control samples, it is questionable if the production of PFOS is due to photolytic activity of the parent material or some unknown impurity.

The Fe_2O_3 data was used as an environmental model to generate a half-life estimate for the degradation of N-EtFOSE alcohol by indirect aqueous photolysis. The additional parameters tested support the proposed mechanism and add to the conditions where the alcohol would be expected to degrade but confuse the rate issue. It is concluded that while the rate is possibly centered around the number of 40 days from the iron oxide data, conditions in the environment could change this rate considerably, possibly by as much as an order of magnitude or more in either direction.

Figure 2. Proposed Degradation Route of N-EtFOSE Alcohol by Indirect Aqueous Photolysis

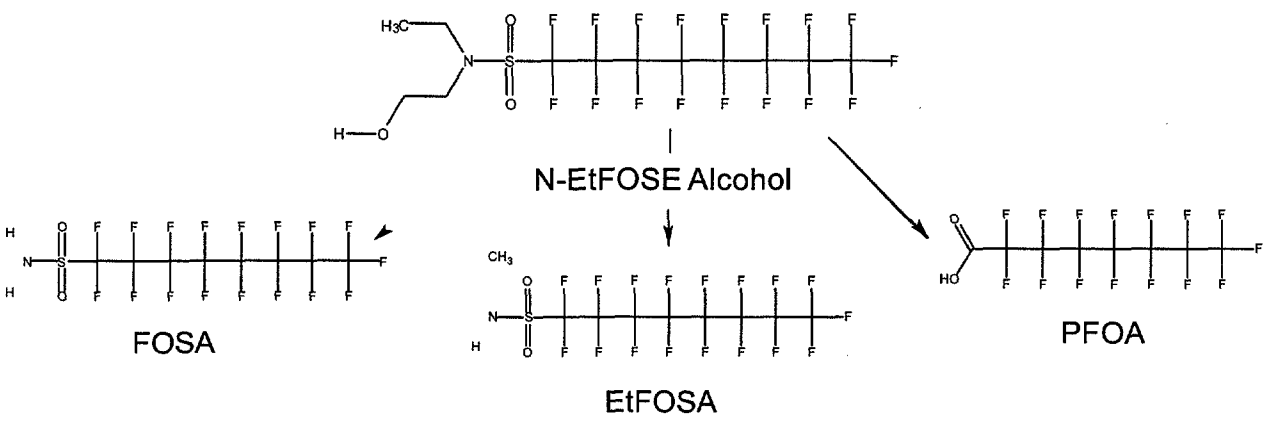


Table 3. Observed Products and Mass Balance Determinations for Photolytic Decomposition of N-EtFOSE alcohol in the Presence of Three Soil Types.

3a. Morgan County - High Clay

Time of exposure was 72.0 hours		ETFOSE-OH	PFOA	PFOS	FOSA	EtFOSA	Mass Balance
Sample	Condition	(nanomoles)	(nanomoles)	(nanomoles)	(nanomoles)	(nanomoles)	(percent)
Soil W/H_2O_2[1]	Initial Time Point	26.35	ND	0.22	ND	ND	87%
Soil WO/H_2O_2[2]	Initial Time Point	27.21	ND	0.23	ND	ND	90%
Soil W/H_2O_2[1]	Exposed to Light	5.22	7.24	0.48	8.16	1.75	75%
Soil WO/H_2O_2[2]	Exposed to Light	23.38	0.84*	0.29	0.78	ND	83%
Soil W/H_2O_2[1]	Not Exposed to Light	25.50	ND	0.26	ND	ND	86%
Soil WO/H_2O_2[2]	Not Exposed to Light	25.85	ND	0.22	ND	ND	84%
Detection Limits		0.92	1.21	0.20	0.21	0.47	

Vials initially contained 30.65 nMoles N-EtFOSE alcohol. 1. Samples contained soil (0.70XX grams in 5 ml water) and H_2O_2 (1:1 molar equivalance H_2O_2:N-EtFOSE alcohol - added every 24 hours), results are from triplicate analysis. 2. Samples contained only soil and analyte, results are from one replicate. *Estimated value ND = non detect.

3b. St. Croix County - Loam

Time of exposure was 72.0 hours		ETFOSE-OH	PFOA	PFOS	FOSA	EtFOSA	Mass Balance
Sample	Condition	(nanomoles)	(nanomoles)	(nanomoles)	(nanomoles)	(nanomoles)	(percent)
Soil W/H_2O_2[1]	Initial Time Point	25.04	ND	ND	ND	ND	82%
Soil WO/H_2O_2[2]	Initial Time Point	24.16	ND	ND	ND	ND	79%
Soil W/H_2O_2[1]	Exposed to Light	8.99	4.81	0.63	1.85	5.03	70%
Soil WO/H_2O_2[2]	Exposed to Light	19.26	2.21	0.55	0.72	1.55	79%
Soil W/H_2O_2[1]	Not Exposed to Light	23.60	ND	0.26	ND	0.43	79%
Soil WO/H_2O_2[2]	Not Exposed to Light	19.62	ND	0.56	ND	ND	66%
Detection Limits		0.92	1.21	0.20	0.21	0.47	

Vials initially contained 30.65 nMoles N-EtFOSE alcohol. 1. Samples contained Soil (0.70XX grams in 5 ml water) and H_2O_2 (3:1 molar equivalance H_2O_2:N-EtFOSE alcohol - added every 24 hours), results are from triplicate analysis. 2. Samples contained only soil and analyte, results are from one replicate. ND = non detect

3c. EPA Synthetic Soil Mix - Sandy Clay Loam

Time of exposure was 72.0 hours Sample	Condition	ETFOSE-OH (nanomoles)	PFOA (nanomoles)	PFOS (nanomoles)	FOSA (nanomoles)	EtFOSA (nanomoles)	Mass Balance (percent)
Soil W/H_2O_2[1]	Initial Time Point	26.17	ND	ND	ND	ND	85%
Soil WO/H_2O_2[2]	Initial Time Point	27.82	ND	ND	ND	ND	91%
Soil W/H_2O_2[1]	Exposed to Light	17.66	3.02	0.72	2.82	2.70	88%
Soil WO/H_2O_2[2]	Exposed to Light	25.54	1.02*	0.25	0.68	0.47	89%
Soil W/H_2O_2[1]	Not Exposed to Light	27.36	ND	ND	ND	ND	89%
Soil WO/H_2O_2[2]	Not Exposed to Light	14.72	ND	ND	ND	ND	48%
Detection Limits		0.92	1.21	0.20	0.21	0.47	

Vials initially contained 30.65 nMoles N-EtFOSE alcohol. 1. Samples contained Soil (0.70XX grams in 5 ml water) and H_2O_2 (3:1 molar equivalance H_2O_2:N-EtFOSE alcohol- added every 24 hours), results are from triplicate analysis. 2. Samples contained only soil and analyte, results are from one replicate. *Estimated value. ND = non detect.

Conclusions

Phototransformations of compounds in the environment not only depend upon such factors as latitude, season, clouds, water clarity etc. but also depend upon the concentrations of other species in the water such as nitrate, iron, and dissolved organics. Photons from a synthetic light source were used to study the photolytic transformations of EtFOSE alcohol. We report here the results of studies to determine the aqueous photolytic stability of 2-(N-ethylperfluorooctanesulfonamido)-ethyl alcohol (*N*-EtFOSE alcohol) and to identify the primary degradation products. Our techniques are based on both EPA and OECD guidance documents.[9,10] In this study, both direct photolysis (the interaction of light with the target molecule leading to a chemical change) and indirect photolysis (the interaction of light with the sample matrix to produce radical species that subsequently react with the target material) were studied using a synthetic light source.

The main findings are that the rate of photodegradation by direct photolysis is negligible, and that the primary products of indirect photolysis are perfluorooctanoic acid, N-ethylperfluorooctane sulfonamide and perfluoroctane sulfonamide. Rates of indirect photolytic degradation are highly dependent on experimental conditions however, using an iron oxide (Fe_2O_3) photoinitiator matrix model an environmental half-life estimate of 40 days was derived. . Dependant upon specific environmental factors, the half-life may vary by at least an order of magnitude in either direction.

Direct photolysis could not be conclusively demonstrated. The indirect light source was used to induce the formation of radicals from the four separate sample matrices (a synthetic humic matrix, a hydrogen peroxide rich matrix, an iron containing matrix and a soil rich matrix). These radical species then reacted with the target to produce new chemical species. Degradation of N-EtFOSE alcohol was observed in each matrix, although the observed rates and product distribution varied from matrix to matrix. Three primary degradation products were observed: PFOA, EtFOSA and FOSA. In several studies, trace levels of additional degradation products were observed, mainly heptadecafluoroctanes and perfluorooctane sulfonate (PFOS). These were detected at trace levels that were close to the quantitation limit. However, it is unclear that either PFOS or the volatiles were the result of degradation of N-EtFOSE alcohol or the result of degradation of low levels (>3% total) of impurities. Mass balance for the degradation of N-EtFOSE alcohol to form the primary products PFOA, EtFOSA and FOSA was within 100±30% for most experimental conditions

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Signatures

The final draft of this report is a true representation of the data developed in this study. It has been issued by:

Thomas L. Hatfield, Ph.D., Special Projects Team Leader — Date 04/20/01

William K. Reagen, Ph. D., Laboratory Management — Date 04/24/01

Appendix A: Analytical Methods

This appendix presents the analytical methods and Standard Operating Procedures used in the present study.

ETS-9-46.0 Operation and Maintenance of the Hewlett Packard 8453 UV-Visible Spectrophotometer

ETS-9-44.0 Operation and Maintenance of the Sunlight Exposure System, Immersion Unit, and Recirculating Water Chiller System

ETS-9-49.0 Routine Maintenance of Archon Purge and Trap Autosampler, Tekmar Purge and Trap Concentrator and Agilent Gas Chromatograph/Mass Spectrometer

ETS-8-177.0 Indirect Photolysis Screening Tests in Synthetic Humic Water

ETS-8-176.0 Preparation of Samples for Photolytic Exposure Studies in Aqueous Matrices

ETS-8-182.0 Analysis of Fluorochemicals by Archon Purge and Trap Autosampler, Tekmar Purge and Trap Concentrator and Agilent Gas Chromatograph/Mass Spectrometer

ETS-8-181.0 Analysis of Photolysis Samples for Fluorochemicals by High Performance Liquid Chromatography With Mass Spectrometry Detection

3M ENVIRONMENTAL LABORATORY

METHOD

ANALYSIS OF PHOTOLYSIS SAMPLES FOR FLUOROCHEMICALS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH MASS SPECTROMETRY DETECTION

Method Number: ETS-8-181.0

Adoption Date: 10/26/00

Exact Copy of Original

JM 3.29.07
Initial Date

Effective Revision Date:

Approved by:

[signature] OCT 26, 00
Laboratory Management Date

[signature] Oct 26, 00
Team Leader Date

1.0 SCOPE AND APPLICATION

1.1 This procedure defines the steps for analysis of fluorochemicals in photolysis study samples by high performance liquid chromatography (HPLC) with mass spectrometry (MS) detection and quantification. Refer to the HP 1100 HPLC/MSD Standard Operating Procedure ETS-9-34.0 for operating and maintenance procedures related to the instrument. Refer to Standard Operating Procedures ETS-8-176 and ETS-8-177 for information involving sample preparation and photolytic exposure procedures.

1.2 **Compatible analytes.** Test substance and degradation products for fluorochemicals or other fluorinated compounds, or other ionizable compounds, which includes but is not limited to:

Compound	Acronym	Compound	Acronym
Perfluorooctanoic acid	PFOA	Perfluorobutanoic acid	PFBA
Perfluorooctanesulfonate	PFOS	Perfluorobutanesulfonate	PFBS
Perfluorooctanesulfonamide	FOSA	Perfluorobutanesulfonamide	FBSA
N-methylperfluorooctanesulfonamide	N-MeFOSA	N-methylperfluorobutanesulfonamide	N-MeFBSA
N-ethylperfluorooctanesulfonamide	N-EtFOSA	N-ethylperfluorobutanesulfonamide	N-EtFBSA
2-(Nmethylperfluorooctanesulfonamido) ethyl alcohol	N-MeFOSE-OH	2-(N-methylperfluorobutanesulfonamido) ethyl alcohol	N-MeFBSE-OH
2-(N-ethylperfluorooctanesulfonamido) ethyl alcohol	N-EtFOSE-OH	2-(N-ethylperfluorobutanesulfonamido) ethyl alcohol	N-EtFBSE-OH
... and other C_4 thru C_{10} homologues, and polymeric materials based on the above aforementioned compounds.			

1.3 **Compatible matrices for analysis.** Aqueous (Millipore ASTM Type I water), buffered water, lake water, sea water and metal slurries (TiO_2, Fe_2O_3, etc.) that have been diluted with an appropriate analytical solvent such as acetone or methanol.

2.0 SUMMARY OF METHOD

2.1 This method describes the analysis of fluorochemicals in a specified matrix, using HPLC electrospray mass spectrometry for chemical separation and detection/quantification. The analysis is performed by separating target analytes on an HPLC analytical column such as a Dionex NG1 (35x 4.6mm, 10μm particle), Betasil C18 column (50X2 mm, 5 μm particle) or equivalent using an ammonium acetate/MeOH solvent gradient. Detection by electrospray ionization mass spectrometery in either the positive or negative mode is utilized to quantify data. The MSD may be run in Selected Ion Monitoring (SIM) mode, looking for specific, pre-selected and set analyte ions (i.e. m/z 499 for PFOS (deprotonated)), or SCAN mode which collects and stores data for all ions in a specified mass range. Data quantification is then performed using either HP ChemStation or Target Software.

3.0 DEFINITIONS

3.1 **Calibration Standard.** A dilution of various amounts of a stock, intermediate or purchased standard to achieve standard solutions in a concentration range of interest.

3.2 **Calibration Curve.** The graphical relationship between known values, such as concentration of a series of calibration standards and their instrumental response.

3.3 **Internal Standard Quantification.** Process of establishing a relationship between the ratio of the target analyte(s) response to internal standard or surrogate response and a known concentration of the target analyte(s). The ratio of analyte to internal standard response is used to generate the calibration curve and determine unknown concentrations.

3.4 **External Standard Quantification.** Process of establishing the concentration of a target analyte by plotting the theoretical amount (in units of ppb or ppm, etc.) versus the response of the target analyte(s) on column. The resultant curve(s) shall be used to determine unknown concentrations by comparing the area response of target analyte(s) to the area response and corresponding analyte amount on the appropriate analyte's calibration curve. Differences in sample mass/volume analyzed, if noted, must be compensated for by a factor applied to the value.

3.5 **Correlation Coefficient (r).** A measure of the degree of correlation between two variables. This term is generally used to evaluate the linearity of a Least Squares Linear regression. An r value of 0.98 is at the lower bounds of what is considered linear. Values of r may range from –1 to +1. A value of +1 denotes perfect direct functional relationship between two variables. A value of –1 also denotes a perfect inverse relationship. When r = 0, there is no effect of one variable upon the other variable.

3.6 **Coefficient of Determination (r^2).** The square of the correlation coefficient. It is the proportion of the variation in the dependent variable that is accounted for by the independent variable.

3.7 **Internal standard.** A known amount of a compound or element similar in analytical behavior to the compound(s) or element(s) of interest, added to all samples and standards, and carried through the entire measurement process (post-photolysis, after solvent dilution). It provides a reference for evaluating and controlling the precision and bias of the applied analytical method. Samples are to be quantified using the internal standard.

3.8 **Surrogate.** An organic compound similar to the target analyte(s) in chemical composition and behavior in the analytical process but is not normally found in the sample(s). A surrogate may be added to samples along with the test analyte (pre and/or post photolysis) to monitor the sample integrity (leaks or matrix effects). The surrogate may be added to the calibration standards to serve as a qualitative reference for the samples.

3.9 **Continuing Calibration Verification (CCV).** Standards analyzed during an analytical run to verify the continued accuracy of the calibration curve. This solution may or may not be prepared from a different source or lot number than the calibration curve standards.

3.10 **Solvent Blank.** A sample of analyte-free medium (for example, methanol, 1:7 diluted buffer:methanol) that is not taken through the sample preparation process. This blank is used to evaluate instrument contamination.

3.11 **Blank.** For photolysis studies, there are multiple blanks to adequately represent the variables of the study (Exposed, Unexposed and Day 0 samples with/without peroxide addition). These blanks are carried through the sample preparation, photolytic and analytical procedures to monitor for contamination during any step. It is also used to establish a chromatographic baseline/background and monitor for analytical interference or suppression of target analyte(s) from the matrix.

3.11.1 **Matrix Blank:** An analyte-free matrix (buffered water, lake water, etc.) to which all reagents are added in the same volumes or proportions as used in sample processing. It is used to document the test system without test analyte present.

3.11.2 **Control Blank:** An analyte-free matrix (ASTM Type II water) to which all reagents are added in the same volumes or proportions as used in sample processing. It serves as a control for the test matrix to monitor background levels, interferences or suppression of target analyte(s) from the test matrix.

3.12 **Limit of Quantitation (LOQ).** The lowest concentration that can be reliably measured within specified limits of accuracy during routine laboratory operating conditions. The LOQ is generally 5 to 10 times the minimum concentration with a 99% confidence limit that the concentration is greater than zero. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes, the LOQ is selected as the lowest non-zero standard in the calibration curve that is greater than 4 times the level of the matrix blank. Sample LOQ are highly matrix-dependent.

3.13 **Sample Triplicates.** Three samples taken from and representative of the same sample source and separately carried through all steps of the extraction, photolysis and analytical procedures in an identical manner. There are multiple sets of triplicate samples to adequately represent the photolytic variables of the study (Exposed, Unexposed and Day 0 with/without peroxide addition). Triplicate samples are used to assess variance of the photolytic method, including sample preparation, photolysis, and analysis.

3.14 **Control Sample.** A known matrix (ASTM Type II water) containing the test analyte(s) carried throughout the entire sample preparation, photolytic and analytical procedure. There are multiple sets of triplicate samples to adequately represent the photolytic variables of the study (Exposed, Unexposed and Day 0 with/without peroxide addition). This is used to document method performance and matrix effects by comparing recoveries from the different matrices and sample types.

3.15 **Relative Standard Deviation (RSD).** A measure of precision defined as the standard deviation of three or more values divided by the average of the values and multiplied by 100. (Also reported as Coefficient of Variation (CV)).

3.16 **Analytical Spike (AS).** Prepared by adding a known mass of target analyte(s) to a specified amount of a sample or control matrix prior to analysis. This assumes that an independent estimate of target analyte concentration is available. Analytical spikes are used to determine the effect of the matrix on recovery efficiency. There are multiple

types of spiked samples to adequately represent the photolytic variables of the study (Exposed, Unexposed and Day 0 ; with/without peroxide addition.)

3.16.1 Matrix Spike. The test matrix (buffered water, lake water) sample containing the test analyte or blank to which a known mass of target analyte(s) is added prior to analysis.

3.16.2 Control Spike. The control matrix (ASTM Type II water) sample containing the test analyte or blank to which a known mass of target analyte(s) is added prior to analysis.

3.17 Accuracy. The closeness of agreement between an experimentally determined value and an accepted reference value. When applied to a set of observed values, accuracy is a combination of a random (precision) and a common systematic (bias) component. For purposes of the study, the acceptance criterion is 75% to 125% of the nominal value.

3.18 Dilution. A step in the sample preparation procedure in which a solvent (i.e. methanol, acetone) is added to the test analyte/sample matrix (i.e. water, buffer, etc.) to prepare it for instrumental analysis.

3.19 Atmospheric Pressure Ionization (API): The Agilent Technologies HPLC 1100/MSD system allows for ionization of incoming liquid sample from the analytical column to the mass spectrometer interface by utilizing a source, probe, hot gas, and specific voltages.

3.20 Electrospray Ionization (ES, ESI): A method of ionization performed at atmospheric pressure, whereby ions in solution are transferred to the gas phase via tiny charge droplets. These charged droplets are produced by the application of a strong electrical field.

3.21 Mass Spectrometry, Mass Spectrometer (MS), Mass Spectrometer Detector (MSD): The API HP1100 MSD system equipped with a quadrupole mass selective detector. Ions are selectively discriminated by mass to charge ratio (m/z) and subsequently detected.

3.22 Geometric Mean of the calibration curve: The square root of the product of the high standard concentration and the low calibration curve standard. When preparing calibration curve standards, the number of calibration standards below the geometric mean shall equal the number of calibration standards above the geometric mean. Having equal distribution of calibration standards above and below the geometric mean when analyzing and reprocessing data, effectively weights the curve such that both the high and low ends of the curve are given equivalent significance.

4.0 WARNINGS AND CAUTIONS

4.1 Health and safety warnings

4.1.1 Wear the proper lab attire for all parts of this procedure. Wear gloves and proper eyewear when performing sample preparation in the laboratory at all times. Wear proper eyewear when working at the instrument in the laboratory.

4.1.2 Handle all solvents in a hood for all parts of the described sample preparation procedure. Whenever possible and practical, dilute samples with solvent in a hood.

4.1.3 For potential hazards of each chemical used, refer to material safety data sheets, packing materials, and the 3M Environmental Laboratory Chemical Hazard Review.

4.2 Cautions

4.2.1 All glassware in which standards are prepared should be rinsed with acetone and methanol to reduce the possibility of contamination.

4.2.2 Ensure that the HPLC mobile phases are prepared prior to beginning a run sequence, and that there is sufficient quantity to complete the run. Do not allow the pump to run dry.

4.2.3 Ensure that before starting the run sequence there is ample hard disk space on the computer to save all run data.

4.2.4 Ensure that there is enough nitrogen in the supply tank to complete sequence runs.

5.0 INTERFERENCE

5.1 Contaminants in solvents, reagents, glassware, and other sample processing or analysis hardware may cause interference. Use the routine analysis of laboratory method blanks to demonstrate that there is no such interference.

5.2 Contamination from columns, HPLC tubing, and detector components may cause interference at low detection levels. The routine analysis of solvent blanks must be used to demonstrate that there is no such interference.

6.0 EQUIPMENT

6.1 Analytical balance sensitive to 0.1 mg.

6.2 Hewlett-Packard (HP) 1100 HPLC System, or equivalent.

6.2.1 Pump, binary, Model G1312; Quaternary, Model G1311A; or equivalent.

6.2.2 Solvent degasser, Model G1322A or equivalent.

6.2.3 Autosampler, ALS Model G1313A, variable injection volume or equivalent.

6.2.4 Column heater, Model G1316A, or equivalent.

6.3 Betasil® C18, 50 x 2 mm; Dionex IonPac® NG1 Guard column, 4 x 35 mm; or equivalent.

6.4 Mass spectrometer. Hewlett-Packard MSD Model G1946A, or equivalent.

6.5 Refrigerator capable of maintaining 4 ± 3 °C.

6.6 Data system. A personal computer capable of controlling the HPLC system as well as recording and processing signals from the detector.

6.7 System control/data analysis software: Hewlett Packard ChemStation®, Version A.6.03 or later.

6.8 Data reprocessing software: Thru-Put Systems Target NT, Revision 4.03, Build 157 or later. Hewlett Packard ChemStation®, Version A.6.03 or later.

7.0 SUPPLIES AND MATERIALS

7.1 Vials, 40 mL, VOA (I-Chem or equivalent)

7.2 Crimp cap autovials, 1.8 mL

7.3 Labels

7.4 Graduated pipets, glass, disposable, 1 mL to 10 mL

7.5 Pasteur pipets, glass, disposable

7.6 Hamilton Gastight® syringes (precision ± 1% of total volume), 10 µL–1000 µL

7.7 Volumetric flasks, various sizes

7.8 Beakers, glass, various sizes

7.9 Automatic pipettor, capable of dispensing 10–5000 µL

8.0 REAGENTS AND STANDARDS

8.1 **Methanol (MeOH).** HPLC/SPEC/GC grade from EM Science, or equivalent

8.2 **Acetone.** HPLC/SPEC/GC grade from EM Science, or equivalent

8.3 **ASTM Type II Water.** Water with lower resistance must not be used.

8.4 **Ammonium acetate, 2 mM in water.** This solution is chromatographic solvent A (see Section 12.2.1). (Example: An acceptable eluent solution is made by adding 0.15 g ammonium acetate crystals to a 1-L volumetric flask containing about 500 mL water, adding 10 mL of methanol, diluting to the mark with 18.0 MΩ water and mixing.)

8.5 **Stock, internal standard, surrogate, post-photolysis spike and calibration solutions**

All weights should be recorded to the nearest 0.0001 g in a standards preparation log:

8.5.1 Fluorochemical or target analyte prepared in acetonitrile (or suitable analytical solvent). (Example: A stock solution is prepared at a concentration of approximately 30,000 µg/mL by weighing 0.3 g of target analyte in a 10-mL volumetric flask and bringing to the mark with suitable analytical solvent. This solution is diluted in solvent to make additional, appropriate standards. Follow specified guidelines for documenting removal of test analyte and target analyte(s), use of balance, preparation of diluted solutions and calibration standards in the appropriate log books. Maintain photocopies of the preparation pages and worksheets in a raw data file.

9.0 SAMPLE HANDLING

9.1 Standards and diluted samples are stored in capped autovials or capped 40 mL VOA vials until analysis.

9.2 If analysis will be delayed, standards and sample extracts may be stored at 4 °C ± 3 °C or room temperature, until analysis can be performed. Document storage conditions on sample prep worksheet with date and initials.

10.0 QUALITY CONTROL

10.1 **Calibration Standards.** Calibration standards (Section 11) used to generate a calibration curve should be prepared in the same type of solvent or matrix as in the study samples. The number of calibration standards and the concentration levels should be sufficient to encompass the expected concentrations of the study samples. In general, a minimum of five calibration standards is required for fit of linear regression. Broad calibration ranges (greater than three orders of magnitude between low and high standards), may require use of a quadratic fit of the data and requires more points to adequately represent the calibration range.

10.2 **Continuing Calibration Verification (CCV).** Analyze a mid-range calibration standard after a maximum of every fifteen samples.

10.3 **Solvent blank.** Solvent blanks are run before and after every calibration curve, CCV, matrix and control blank (if contamination is noted), and after batches of no more than 30 injections. Acceptable values for the blanks are values below 25% of the limit of quantitation (LOQ) of the instrument. If analyte carryover is a problem, use back-to-back solvent blanks.

10.4 **Sample Triplicates.** Analyze all sets of triplicate samples to provide a measure of the precision of analysis. Study samples will be analyzed in batches of no more than 30 samples. Multiple batches in an analytical sequence will be bracketed by calibration standards at the beginning and end of each study sample batch. All samples (matrix and control samples, blanks and spikes) from a specified exposure type or time may be analyzed within the same analytical batch.

10.5 **Analytical spikes.** Prepare analytical spike sample for each sample type as applicable to determine the matrix effect on the recovery efficiency. Concentrations of the spike should be approximately equal to a mid-range calibration standard. The matrix spike sample should be analyzed periodically to measure the precision associated with the analysis. The analyst shall accept percent spike recoveries of 100 ± 25%. Spike recoveries outside of this range should be noted and used with other criteria to evaluate the condition of the analytical run or necessity for repeat analysis. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run. Samples may be spiked at two different concentrations to ensure that the resulting levels of target analyte(s) are within the viable range of the calibration curve.

11.0 CALIBRATION AND STANDARDIZATION

11.1 Analyze standards prior to and following each set of samples. The linear regression will be calculated from the plot of all individual calibration points, including but not forced through zero, using HP ChemStation or Target NT Software. A minimum of five calibration standards is required to generate linear regression for target analyte(s). If the calibration curve residuals are greater than 25% deviation from the theoretical value, quadratic curve fitting and/or dropping low/high curve points may be required if data review shows this to be a consistent and more accurate representation of the instrument response. Document in the raw data the technical justification for any deviation and consult with the team leader or designee for direction and for final acceptance or rejection of the data.

11.1.1 Use the following documentation/footnotes may be used to justify dropping high/low curve points.

1) "High/low calibration points (list points) were excluded to provide a better fit over the linear range appropriate to the measured data."

2) "Low level calibration point(s) were not 4x higher than the extraction blank; these points were excluded from the curve to disqualify a data range that may have been significantly affected by background levels of the analyte."

3) "High/low calibration point(s) (list points) were excluded as they were not within the +/-25% accuracy requirements of the method when the curves were evaluated over a linear range appropriate to the data.'

11.2 If the curve does not meet requirements perform routine maintenance or prepare a new standard curve (if necessary) and reanalyze.

12.0 PROCEDURES

12.1 **Instrument set up.** Within "Method and Run Control" in the HP ChemStation Software window, turn the system "on" to: turn on the drying gas flow; initiate solvent flow through the column and nebulizing needle; equilibrate the column compartment; and equilibrate the MSD spray chamber temperatures and conditions. The system module displays should turn a green color to indicate the instrument is "ready" for analysis. A yellow color indicates that the system is not ready, but is working to "get ready." A red colored module icon indicates a type of systematic failure and should be corrected prior to proceeding. Check the run log for error messages and error codes if the problem is not apparent.

12.2 **MSD set-up.** Turn the MSD "on" in the software to equilibrate the system.

12.2.1 Check the level of nitrogen in the tank and ensure there is enough to complete the impending run.

12.2.2 Clean the MSD according to the Equipment Procedure ETS-9-34.0 Operation and Maintenance of HP LC/MS System.

12.2.3 Perform a Check Tune or Autotune to ensure system operational qualification and performance verification of the MSD. Log the Tune results and keep a copy with the analytical raw data.

12.2.4 Load the method file and ensure that the following parameters are appropriately set for the target analyte(s):
Example mass spectrometer set up*:

MSD:	Ionization mode	API-ES (or API-APCI)
	Polarity	Negative (or Positive)
	Acquisition mode	SIM (or SCAN)
	Gain	1.0 (up to 7.0)
	Fragmentor	70 (may be set to one voltage, or ramped for each ion)
	Dwell time	183 msec (time is a function of the amount of ions).
	Capillary voltage	3500, or equivalent
	Drying gas	Nitrogen, or equivalent
	Nebulizer pressure	30 psig, or equivalent
	Drying gas flow	8 L/min, or equivalent
	Drying gas temp	300° C, or equivalent

*Example conditions are applicable to HP1100 LC/MSD equipment only.

12.3 LC Check

12.3.1 Check that the appropriate HPLC column is in the instrument for analysis.

12.3.2 Check that the correct eluent solutions are in bottles to be used and that enough is available to complete the sequence run. Adjust the solvent bottle level electronically within the method and run control window.

12.3.3 Ensure that the method file has the appropriate LC pump parameters for solvent flow/gradient program , column I.D/temperature, injection volume and stop time.

Solvent A: Ammonium Acetate 2mM in water (with 1% MeOH) (or equivalent).

Solvent B: Methanol (or equivalent).

Example Solvent Gradient:

TIME (MIN)	%A	%B	FLOW RATE
0.0	60	40	0.3 mL/min
1.0	60	40	0.3 mL/min
4.0	5	95	0.3 mL/min
11.0	5	95	0.3 mL/min

Post time: 6 minutes, column temperature: 35°C.

The initial solvent composition is set to a higher amount of aqueous solvent so as to achieve sufficient sample retention on the column. The gradient composition

increases to a higher organic content over time to separate the analytes, and elute them off the column in a timely fashion. After all analytes have eluted, the solvent ratio is then switched back to "initial conditions" and held until the column pressure has stabilized (indicating re-equilibration to initial conditions) prior to the next injection.

12.3.4 Auto-sampler setup:

AUTO-SAMPLER:	ALS Model G1313A
AUTO-SAMPLER PROGRAM:	None
INJECTION VOLUME:	5.0 µL, or equivalent

*Example conditions are applicable to Hewlett Packard 1100 LC/MSD only

12.3.5 Place the samples in the autosampler tray and construct a sequence table with appropriate calibration standards, calibration check standards and solvent blanks.

12.3.5.1 Verify that all samples and standards are positioned correctly.

12.3.5.2 Enter the identification code for each standard and samples. For solvent blanks, identify the solvent and the traceability number.

12.3.5.3 Use one injection per sample.

12.3.5.4 Ensure the method file is correctly entered for all samples.

12.4 Sequence and electronic storage of data files.

12.4.1 Within the sequence parameters, enter sequence information (brief sample population description and instrument name).

12.4.2 Set post-sequence command macro to shut down system after the run is completed (Example: "STANDBY" on HP1100/MSD systems).

12.4.3 Save all data to a subdirectory labeled with instrument and analysis date (e.g. H100200 for analysis on "Hillary," on 2 October, 2000).

12.4.4 Name data within the subdirectory with instrument ID and injection/run number (e.g. for samples acquired on "Hillary", data files shall be "HILL0001".... "HILL00##"). DO NOT exceed five identification characters for analysis of more than 99 samples since eight characters total are available for sample ID, and the last three digits are for sample numbering purposes (leaving the first five characters for data file identification).

12.4.5 Save sequence as analysis date and instrument letter (e.g. For analysis on instrument "Hillary" on October 2, 2000 save sequence table as H100200.s).

12.5 Sample analysis

12.5.1 Enter the standard, sample, blank identification into the sequence table. Analyze calibration standards first, then up to 30 injections, followed by the calibration standards re-injected. Multiple sets of samples can be set up in the sequence table with each set bracketed by calibration standards. Analyze a single continuing calibration standard (CCV) after a maximum of 15 injections. Solvent blanks shall be analyzed before and after the CCV and before method and control blanks, if

necessary. Two solvent blanks shall be analyzed at the end of the calibration standards to ensure that there is no carry over from the highest standard concentration. Solvent blanks may also be used to separate groups of samples and evaluate for carry over problems from actual samples. Ensure standards, blanks, samples, and matrix spikes in the auto-sampler tray vials are in same order as listed in the sequence.

12.5.2 Print a copy of the tune results, method and sequence to be stored with raw data.

12.5.3 Start the sequence.

12.6 **Post Analysis.** Prepare a folder identified specifically to the project and save data, method and sequence files. This will be considered the raw electronic data to be archived.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 **Peak Evaluation.** Peaks must be symmetric in shape and identified by extracting compound-specific ions. Peaks considered for quantification must have peak heights greater than 4 times any baseline level for that region of the chromatogram. Peak area integration is from baseline to baseline using automatic or manual integration. Manual integration is not acceptable for calibration standards and should only be used in extreme cases as designated by the Team Leader. Samples and standards that may need to be manually integrated must be documented in the raw data as to why the peak was manually integrated.

13.2 **Integration Codes.** The following integration codes may be utilized to document what type of manual integration was performed.

A: Adjust Left Anchor B: Adjust Right Anchor
C: Delete Integration D: Add Integration

Additionally, QAU encourages the data reviewer to write comments directly on the chromatogram if there is anything unusual. Date and initial all documentation.

13.3 **Matrix spikes.** Calculate the percent recovery for each of the matrix spikes. Calculate the matrix spike percent recoveries using the following equation:

$$\% \text{ Recovery} = \frac{(\text{observed spiked sample result} - \text{observed sample result})}{\text{Nominal amount spiked}} \times 100$$

Using the observed matrix spike recoveries, calculate the average spike recovery.

13.4 **Accuracy.** Calculate the accuracy of each calculated calibration standard and CCV samples using the following equation.

$$\text{Accuracy} = \frac{(\text{Measured Conc.})}{\text{Nominal Conc.}} \times 100$$

13.5 Sample Triplicates. Calculate the relative standard deviation (%RSD) for the triplicate samples:

$$RSD = \frac{\text{Standard Deviation of Sample Set}}{\text{Average of Sample Set}} \times 100$$

14.0 METHOD PERFORMANCE

14.1 Coefficient of Determination (r^2). The coefficient of determination (r^2) for the calibration curves should be 0.990 or greater. The curves should be examined closely for linearity and intercept, particularly for accuracy of quantitation at the low and high ends of the curve. The accuracy of all standards used for calibration must be within 75-125%. It may be necessary to use quadratic fits of the data, usually when broad range curves (greater than 3 orders of magnitude between the low and high concentration standards) are used. Document in the raw data the technical justification for using quadratic equations. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.2 Calibration Standards. The acceptance criterion for the calibration standards is that the accuracy of each standard is 75% to 125% (± 25 % difference) of the nominal value. Calibration standards outside this range are to be noted. Document in the raw data the technical justification for deviations. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.3 Internal Standard (IS) and Surrogate. Review of the internal standard and surrogate performance is performed by averaging the area response throughout the analytical run and calculating %RSD. Inconsistencies in the internal standard peak area may indicate instrumental changes over time. Inconsistencies in the surrogate peak area may indicate instrumental changes, injection error, or changes in the test-system. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run.

14.4 Continuing Calibration Verification. If the accuracy for the amount of measured analyte is greater than 25% from the nominal value relative to the initial standard curve, the Team Leader should be consulted. Only those samples analyzed before the last acceptable calibration check standard may be used. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.5 Solvent Blanks. Solvent blanks should show no more than a 5% carryover from a high standard or calibration check standard. If so, two solvent blanks may be necessary to rule out instrumental contamination. If peaks greater than 25% of the peak area of the designated LOQ value are observed in sequential solvent blanks, this is indicative of instrument contamination. The instrument shall be serviced by thoroughly cleaning the electrospray source, and replacing/cleaning columns, tubing, etc. (as designated in the Equipment Procedure, ETS-9-34.0) and the analysis restarted. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run.

14.6 Matrix Blanks. Matrix blanks are the basis for determining the LOQ and are monitored at various times in the analytical run. Samples with greater than 25% of the peak area of the designated LOQ value observed in matrix blanks are indicative of matrix effect,

sample contamination or instrument contamination. Evaluation of the solvent and control blanks may be necessary to determine these effects. Use of solvent blanks prior to the matrix blank may be necessary to rule out instrumental or sample contamination.

14.7 **Control Blanks.** Control blanks are the basis for determining matrix effect (interference or suppression) and also to monitor for instrumental or sample contamination. Use of solvent blanks prior to the matrix blank may be necessary to rule out instrumental or sample contamination.

14.8 **Limit of Quantitation (LOQ).** The LOQ is equal to the lowest acceptable standard (i.e. % accuracy is ≤ 25 % nominal value) in the calibration curve that is greater than 4 times the level of the matrix blanks.

14.9 **Sample Triplicates.** The analyst shall accept %RSD values < 25%. %RSD values > 25% should be noted . Data used in the final report that is deemed out of control will be required to have technical justification for why the data is used, documented in the final report and raw data. Consult with the Team Leader or designee for direction, and for final acceptance or rejection of the data.

14.10 **Control Samples.** The acceptance criterion for the control samples is that the accuracy is 75% to 125% of the nominal value. These will be used as a reference for matrix effect and overall method performance. Control samples outside this range are to be noted. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data. Data used in final report that is deemed out of control will be required to have a technical justification for why the data are being used, documented in the final report and raw data.

14.11 **Analytical Spikes.** The analyst shall accept percent spike recovery values of 100 ± 25%. Spike recoveries outside of this range should be noted. Consult with the Team Leader or designee for direction, and for final acceptance or rejection of the data. Data used in final report that is deemed out of control will be required to have a technical justification for why the data are being used, documented in the final report and raw data.

14.12 **System Suitability.** Without performing a method validation, system suitability can be demonstrated by acceptable instrumental checks (e.g. abbreviated m/z check-tune, or full auto-tune routines. Consult the appropriate instrumental manuals (Reference 18.2). Furthermore, overlaying calibration curves and implementing check standards (CCV), the method shall be self-validating if all data quality objectives are satisfied.

15.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 Dispose of sample waste by placing in high or low BTU containers as appropriate. Use broken glass containers to dispose of glass pipettes.

15.2 Collect HPLC solvent waste in the satellite accumulation can. Empty into the flammable storage drum in the hazardous waste collection area on the 2nd floor.

15.3 Use smaller bore columns when possible to minimize waste generation.

16.0 RECORDS

16.1 Print hard copies of all graphics and data analysis summaries for archiving.

16.2 Sign and date all graphics and label with instrument ID.

16.3 Fill out appropriate preparation worksheets completely, making sure to include all initials and dates, along with the study number and sample identification.

16.4 Print out the sample acquisition sequence table, reduce the size with photocopying and tape the photocopy into the instrument log. Keep the original copy for the raw data files.

16.5 Print chromatograms, reprocessing sequence and batch reports for all analyses.

16.6 Print calibration tables and curve information and store in the raw data file.

16.7 Enter all standard preparation information in the standards preparation logbook. Make a photocopy of the logbook page and include the copy in the raw data file.

16.8 Archive electronic data to appropriate media when necessary.

17.0 ATTACHMENTS

17.1 None.

18.0 REFERENCES

18.1 ETS-9-34.0, Hewlett Packard 1100/MSD Equipment Procedure.

18.2 Hewlett Packard 1100/MSD instruction CD/ROM.

19.0 AFFECTED DOCUMENTS

19.1 None.

20.0 REVISIONS

Revision number	Reason for revision	Date of Revision

3M ENVIRONMENTAL LABORATORY

Method

Preparation of Samples for Photolytic Exposure Studies in Aqueous Matrices

Method Number: ETS-8-176.0 **Adoption Date:**

Approved By:

Laboratory Manager 03/26/01 Date

Team Leader March 26, 01 Date

Exact Copy of Original

JAM 3-29-01

Initial Date

1.0 SCOPE AND APPLICATION

1.1 **Purpose.** Chemicals dissolved in aqueous solutions are subject to two types of photoreaction. The first type (direct photolysis) occurs when the chemical of interest absorbs sunlight directly and is transformed to products when unstable, excited states of the molecule lead to decomposition. The second type is indirect photolysis, where degradation of the dissolved chemical is the result of chemical or electronic excitation transfer from light-absorbing species in the water. The simplest reaction involves the absorption of UV energy by hydrogen peroxide (H_2O_2) to produce 2 hydroxl radicals. These may react with any species in the water, including solvent, buffer, dissolved organic material and target material. Use of water and H_2O_2 is very controlled and predictable. Other sources in other matrices are not as controlled or predicable, but are more environmentally relevant.

Natural waters such as lake and sea water can be used for the photolytic reaction matrix because it may contain dissolved organic material that absorbs sunlight and produces reactive intermediates that include singlet oxygen ($^1O_2$) which may promote indirect photolysis of the test substance. Another transient species photochemically produced by the reaction of UV light and dissolved organic materials (humic) is hydrogen peroxide (H_2O_2) which may react further to form the hydroxyl radical. The addition of H_2O_2 to test solutions may be utilized as a free radical source to initiate indirect photolytic reactions in controlled test solutions such as MilliQ water or buffers. Further studies involving the use of either naturally occurring metal complexes such as Fe(III) which undergo photoreduction to Fe(II) and free radicals or addition of TiO_2 as a catalytic surface for indirect photolysis may also be evaluated within this method.

1.2 **Compatible analytes.** Test substance and degradation products for photolytic exposure include but are not limited to:

Compound	Acronym	Compound	Acronym
Perfluorooctanoic acid	PFOA	Perfluorobutanoic acid	PFBA
Perfluorooctanesulfonate	PFOS	Perfluorobutanesulfonate	PFBS
Perfluorooctanesulfonamide	FOSA	Perfluorobutanesulfonamide	FBSA
N-methylperfluorooctanesulfonamide	N-MeFOSA	N-methylperfluorobutanesulfonamide	N-MeFBSA
N-ethylperfluorooctanesulfonamide	N-EtFOSA	N-ethylperfluorobutanesulfonamide	N-EtFBSA
2-(N-methylperfluoro octanesulfonamido) ethyl alcohol	N-MeFOSE-OH	2-(N-methylperfluorobutanesulfonamido) ethyl alcohol	N-MeFBSE-OH
2-(N-ethylperfluorooctanesulfonamido) ethyl alcohol	N-EtFOSE-OH	2-(N-ethylperfluorobutanesulfonamido)ethyl alcohol	N-EtFBSE-OH
1-perfluorooctene	—	1-perfluorobutene	---
Perfluorooctanehydride	1H, C_8-hydride	Perfluorobutanehydride	1H, C_4-hydride
... and other C_4 thru C_{10} homologues, and polymeric materials based on the aforementioned compounds.			

Other possible degradation products include, but are not limited to:

C_2	1H-perfluoroethane (1H-pfC2)	1H-perfluoroethane (1H-pfC2)		
C_3	1H-perfluoropropane (1H-pfC3)	2H-perfluotopropane (2H-pfC3)	perfluoro-1-propene (pfC3-1ene)	
C_4	perfluoro-1-butene (pfC4-1ene)	Perfluoro-2-butene (pfC4-2ene)	2H-perfluorobutane (2H-pfC4)	1H-perfluorobutane (1H-pfC4)
C_5	2H-perfluororpentane (2H-pfC5)	perfluoro-1-pentene (pfC5-1ene)	perfluoro-2-pentene (pfC5-2ene)	
C_6	perfluoro-2-hexene (pfC6-2ene)	1H-perfluorohexane (1H-pfC6)	perfluoro-1-hexene (pfC6-1ene)	1H-perfluorohexane (1H-pfC6)
	2H-perfluorohexene (2H-pfC6)			
C_7	2H-perfluoroheptane (2H-pfC5)	Perfluoro-1-heptene (pfC7-1ene)	1H-perfluoroheptane (1H-pfC7)	
C_8	perfluoro-1-octene (pfC8-1ene)	2H-perfluorooctane (2H-pfC8)	Perfluoro-2-octene (pfC8-2ene)	1H-perfluorooctane (1H-pfC8)

1.3 Acceptable matrices. Aqueous solution of test substance including but not limited to the following matrices: pH 7 phosphate buffer, 18.2 MΩ resistivity water, seawater and metal solutions.

2.0 SUMMARY OF METHOD

2.1 The objective of the photolytic exposure study is to determine whether the test substance undergoes degradation by either direct or indirect photolysis, and to identify and quantify degradation products formed in the test matrix under these conditions. Study samples (5 mL aqueous matrix) are prepared in 40 mL glass VOA vials equipped with screw-top caps with septa. Study sets are prepared in duplicate for separate analysis by LC/MS and dynamic purge and trap GC/MS. When required, the addition of 30% H_2O_2 solution to initiate radical formation is performed prior to the photolytic exposure and at specified intervals throughout the exposure study. Vials are placed in the photo-reactor and immersed in a water bath controlled at 23-26 °C. Samples are exposed to approximately 261 W/m^2 of 310-800 nm photo-irradiance for a specified number of 8-hour periods. An 8-hour period of irradiance is defined as one day's worth of sunlight. Other parameters are acceptable, with the time and settings noted for each study. The number of days to expose samples is determined by the Team Leader. The amount of irradiation received by the samples may be monitored in one of the following three ways: 1) calculating the total wattage per length of exposure 2) use of a radiometer to measure irradiance output, and/or 3) use of a quinine monohydrochloride dihydrate (QMD) actinometer solution exposed along with the samples and monitored for change in UV absorption over time. The use of the radiometer provides an accurate measurement at specified time-points; whereas calculating the total wattage per exposure length and use of the QMD actinometer provide time-averaged total integrated energies. Suntest instruments contain an internal radiometer for maintenance of constant irradiance. A second radiometer may be used as a check for consistency. At the end of the exposure time, samples are removed from the photoreactor and either subsequently analyzed or stored at 1-5 °C. Study samples to be analyzed by LC/MS are prepared for analysis by diluting the 5 mL sample volume with 30 mL of suitable analytical solvent (e.g. methanol) containing internal standard. The GC/MS study samples are stored inverted prior to purge and trap GC/MS analysis.

2.2 An example of samples to be prepared for each study is shown in the table below. Exact lists may vary, dependent upon the test specifics for each study and will be noted in individual study reports. Typically, there are extra control samples for certain matrices such as Fe_2O_3.

						LC/MS		GC/MS	
Description	Test Matrix	Control Matrix	Test Substance	Post Photolysis Target Analyte spike	Sample Type	With H_2O_2	Without H_2O_2	With H_2O_2	Without H_2O_2
Sample Rep 1	+	0	+	0	Time 0	X	X	X	X
Sample Rep 2	+	0	+	0	Time 0	X	X	X	X
Sample Rep 3	+	0	+	0	Time 0	X	X	X	X
Sample Spike	+	0	+	+	Time 0	X	X	X	X
Matrix Blank	+	0	0	0	Time 0	X	X	X	X
Matrix Blank Spike	+	0	0	+	Time 0	X	X	X	X
Control Sample	0	+	+	0	Time 0	X	X	X	X
Control Spike	0	+	+	+	Time 0	X	X	X	X
Control Blank	0	+	0	0	Time 0	X	X	X	X
Control Blank Spike	0	+	0	+	Time 0	X	X	X	X
Sample Rep 1	+	0	+	0	Exposed	X	X	X	X
Sample Rep 2	+	0	+	0	Exposed	X	X	X	X
Sample Rep 3	+	0	+	0	Exposed	X	X	X	X
Sample Spike	+	0	+	+	Exposed	X	X	X	X
Matrix Blank	+	0	0	0	Exposed	X	X	X	X
Matrix Blank Spike	+	0	0	+	Exposed	X	X	X	X
Control Sample	0	+	+	0	Exposed	X	X	X	X
Control Spike	0	+	+	+	Exposed	X	X	X	X
Control Blank	0	+	0	0	Exposed	X	X	X	X
Control Blank Spike	0	+	0	+	Exposed	X	X	X	X
Sample Rep 1	+	0	+	0	Unexposed	X	X	X	X
Sample Rep 2	+	0	+	0	Unexposed	X	X	X	X
Sample Rep 3	+	0	+	0	Unexposed	X	X	X	X
Sample Spike	+	0	+	+	Unexposed	X	X	X	X
Matrix Blank	+	0	0	0	Unexposed	X	X	X	X
Matrix Blank Spike	+	0	0	+	Unexposed	X	X	X	X
Control Sample	0	+	+	0	Unexposed	X	X	X	X
Control Spike	0	+	+	+	Unexposed	X	X	X	X
Control Blank	0	+	0	0	Unexposed	X	X	X	X
Control Blank Spike	0	+	0	+	Unexposed	X	X	X	X

+ = added to test vial; 0 = NOT added to test vial; X = One set w/H_2O_2, One set w/o H_2O_2

3.0 QUALITY CONTROL-DEFINITION/FREQUENCY/PERFORMANCE CRITERIA

3.1 Blanks

3.1.1 *Definition:*

Matrix Blank. An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. For photolysis studies, there are multiple matrix blanks to adequately represent the variables within the study in reference to the matrix (e.g. Exposed, Unexposed, Time 0; with peroxide, without peroxide). The matrix blanks are carried through the complete sample preparation, experimental treatment and analytical procedure. The matrix blank is used to document contamination resulting from the experimental treatment and analytical process. Refer to the table below for an example of matrix blank types. The matrix blank is used to document the actual test system without the test substance. The control blank is used to control the test matrix and trace any background levels of target analyte that may be matrix-specific. The table below shows an example of a control blank

3.1.2 ***Performance Criteria:*** The frequency of use and the performance specifications for each of the above defined method blank types shall be as follows:

Matrix ID	Matrix description	Frequency	Performance Criteria
Matrix Blank	Example: 0.01 M Phosphate Buffer, pH 7	**1 Replicate** per light and dark exposure, for each time point and for each analytical methodology.	Any background level of target analyte shall be less than 25% the area counts of the LOQ.
Control Blank	Example: ASTM Type II Water		

3.2 Limit of Quantitation (LOQ)

3.2.1 Definition: The lowest concentration that can be reliably measured within specified limits of accuracy during routine laboratory operating conditions. Sample LOQs are highly matrix-dependent.

3.2.2 ***Quality Control and Performance Criteria:*** The LOQ is generally 5 to 10 times the minimum concentration with a 99% confidence limit that the concentration is greater than zero. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes, the LOQ is selected as the lowest non-zero standard in the calibration curve that is greater than 4 times the level of the solvent blanks and indicates good accuracy (± 25%) of the nominal calibration standard concentration.

3.3 Sample Triplicate

3.3.1 ***Definition:*** Three aliquots prepared as representatives of the same sample source (i.e. test substance) and carried through all steps of the photolytic study process and analytical procedures in an identical manner. The results from triplicate analyses are used to evaluate variability of the total method, including sample preparation, photolytic process and analysis.

3.3.2 ***Performance Criteria:*** The samples in the test matrix will be prepared in triplicate. Each replicate will be prepared for each treatment type: light and dark exposures, with and without hydrogen peroxide, for EACH time-point, and for each analytical methodology (e.g. LC/MS and/or GC/MS). See the following table:

Matrix Description	Frequency of Use	Performance Criteria
Test Matrix *containing* test analyte(s)	**3 Replicates** per light AND dark exposure, with AND without H_2O_2, for each time-point, and for each analytical methodology (i.e. LC/MS and/or GC/MS).	The analyst shall accept %RSD <25%. Precision values not meeting specification must be documented and justified (if possible).

3.4 Control Sample

3.4.1 ***Definition:*** A known matrix containing the test analyte(s) carried throughout the entire analytical procedure. This is used to document laboratory performance (i.e. precision of sample preparation by comparing spike recoveries from the different matrices and sample types). A control sample consists of a control matrix spiked with test analyte(s). A control sample should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process

are within control limits. The results of control sample analyses are compared to control limits established for both precision and bias to determine usability of the data.

3.4.2 ***Performance Criteria.*** One control sample will be prepared per matrix, per treatment type. See the following table:

Matrix Description	Frequency of Use	Performance Criteria
Control matrix *with* test analyte(s) added	**1 Replicate** per light AND dark exposure, with AND without H_2O_2, for each time-point, and for each analytical methodology (i.e. LC/MS and/or GC/MS).	The analyst shall accept recovery values of 100 ± 25%. Accuracy values not meeting specification must be documented and justified (if possible).

3.5 Analytical Spike (AS)

3.5.1 ***Definition:*** Prepared by adding a known mass of target analyte(s) to a specified amount of a diluted and/or aliquoted sample. This assumes that an independent estimate of target analyte concentration is available. Analytical spikes are used to evaluate the recovery efficiency of the analyte and the effect of the matrix on the measurements.

3.5.2 **Quality Control and Performance Criteria:** One sample spike will be prepared in the actual test matrix sample, and one control spike in the control matrix will be prepared. Each replicate will be prepared per treatment type: for light and dark exposures, with and without hydrogen peroxide, for each time-point, and for each analytical methodology (i.e. LC/MS and/or GC/MS). In addition, one matrix blank spike and one control blank spike will be prepared. See the following table:

Matrix Description	Frequency of Use	Performance Criteria
Test Matrix *and* test substance, spiked with target analyte(s) just prior to analysis	**1 Replicate** per treatment type.	The analyst shall accept spike recovery values of 100 ± 25%. If spike recoveries are greater than 125% or less than 75%, document that the spike sample is out of the specifications and justify, if possible, the reason.
Control Matrix *and* test substance, spiked with target analyte(s) just prior to analysis	**1 Replicate** per treatment type.	
Test Matrix *without* test substance, spiked with target analyte(s) just prior to analysis	**1 Replicate** per treatment type.	
Control Matrix *without* test substance, spiked with target analyte(s) just prior to analysis	**1 Replicate** per treatment type.	

3.6 Internal Standard/Surrogate

3.6.1 ***Internal Standard Definition (applies to LC/MS and GC/MS samples):*** A known amount of a compound similar in analytical behavior to the target analyte(s) of interest, added to all samples and standards (post-irradiation), and carried through the entire analytical process. It provides a reference for evaluating and controlling the precision and bias of the applied analytical method. Samples are

to be quantified using the internal standard providing that the response of the internal standard is consistent (± 5% relative). Use of external calibration methodology requires written justification by the Team Leader.

3.6.2 ***Surrogate Definition (applies to LC/MS and GC/MS samples):*** A known amount of a compound similar in analytical behavior to the target analyte(s) of interest may be added to all samples and standards (pre- or post-irradiation, at the discretion of the Team Leader) and carried through the remaining sample preparation and analytical process. If added before exposure, it monitors the presence of vial leaks during photolysis, as well as the performance of the purge and trap auto-sampler and concentrator. Surrogate analysis is used to evaluate and control the precision and bias of the analytical method. Surrogates are not used for quantitation.

Note: Internal standards are used in all experiments. The use of surrogate standards may or may not be used.

3.6.3 Quality Control and Performance Criteria:

Matrix Description	Frequency of Use	Performance Criteria
Sample diluted with 30 mL of **internal standard** compound dissolved in a suitable analytical solvent	Every **LC/MS** sample analyzed	The Coefficient of Variation, or %RSD shall be calculated for the area response of all appropriate samples per analytical batch. The analyst shall accept %RSD values of <15%. The recovery and precision of the surrogates should be 100 ±25% and <15%, respectively. Unacceptable values shall be documented and justified, if possible.
Sample with **surrogate** compound spiked into it.	Every **GC/MS** sample analyzed	

3.7 Other Definitions.

3.7.1 Test Analyte/Substance: Any substance (mixture or controlled compound) added or administered to the test system for the purpose of chemical analysis.

3.7.2 Degradation Product(s): Secondary analytes of interest produced as a result of chemical reactions during the photolysis and monitored (qualitatively or quantitatively) during the sample analysis procedure.

3.7.3 Target Analyte(s): The analyte(s) singled out in the analytical phase of the study is the target analyte. The target analyte may be identical to the test substance used in the experimental phase of the study, a by-product or degradation product that is monitored (qualitatively or quantitatively) during the sample analysis procedure.

3.7.4 Test Matrix: The physical matrix in which the study will be conducted. Also referred to as the test system.

3.7.5 Control Matrix: A known physical matrix to be included with the study for comparison with the test matrix.

3.7.6 Relative Standard Deviation (RSD): A measure of relative precision for three or more sample replicates; defined as the sample standard deviation divided by the sample average and multiplied by 100. This is expressed as percent (%RSD).

3.7.7 Accuracy: The closeness of agreement between an experimentally determined value and an accepted reference value; defined as the measured value divided by the nominal value and multiplied by 100.

4.0 HEALTH AND SAFETY WARNINGS

4.1 Safety

4.1.1 Wear the proper lab attire, gloves and eye protection for all parts of these procedures.

4.1.2 Handle all solvents in a hood for all parts of the described sample preparation procedure.

4.1.3 For potential hazards of each chemical used, refer to material safety data sheets, packing materials, and 3M Environmental Laboratory's Chemical Hazard Review.

4.1.4 No mouth pipetting is allowed.

4.2 Cautions

4.2.1 Glassware in which standards are prepared should be rinsed with solvent to reduce the possibility of accidental contamination.

4.2.2 The photoreactors are equipped with a continuous flow of cooling water, which poses a threat of electrocution during the handling of the photoreactor during irradiation sequences. To avoid possible injury, inspect the units frequently for water leakage and electrical outlets and wiring for wear and tear. Replace any worn parts immediately.

4.2.3 Wear dark protective eyewear when operating the reactor. Do not look directly at the activated lamp. Use caution when handling samples in the reactor; the interior walls of the reactor and exposed glass vials become extremely hot.

5.0 Interference

5.1 Solvents, water and matrix components could interfere with detection thereby decreasing sensitivity in the sample analysis. Care must be taken to prevent all possible contaminants by using fresh reagents, analytical grade solvents and clean glassware during the sample preparation processes.

6.0 EQUIPMENT

6.1 Analytical balance sensitive to 0.1 mg

6.2 Photoreactor: Suntest CPS+, XLS+, or equivalent, equipped with a xenon arc-lamp and capable of producing integrated irradiance values from 100-680 W/m^2 over the wavelength range of 290-800 nm. Lamp output must be filtered to allow only 290-800 nm wavelengths. A flowing water bath with circulating pump is required. Consult the appropriate 3M SOP for instructions.

6.3 Water recirculating cooler capable of maintaining temperature at 25 °C ± 5 °C, from Poly Science, Model 1177-P or equivalent.

6.4 Agilent Technologies UV-visible Spectrophotometer, equipped with tungsten and deuterium lamps, Model 8453, or equivalent. Consult the appropriate 3M SOP for instructions.

6.4.1 Autosampler equipped with eight sample cell holders: Agilent Technologies Model G1120A, Thermostatted Cell Holder: Model 08451-60104, or equivalent.

6.4.1.1 1.0-cm path length quartz spectrophotometer cell from Hewlett Packard, or equivalent.

6.4.2 Long Path-Length Cell Holder, Hewlett Packard (# 89076C) or equivalent.

6.4.2.1 10-cm path length quartz cell equipped with stopcocks, Hewlett Packard Part # 5061-3392, or equivalent.

6.4.3 Data acquisition and analysis software, HP ChemStation for UV-Visible Spectroscopy, G1116AA, Rev. B.01.02, or later.

6.4.4 PC Computer capable of running appropriate analysis software to acquire and report data.

6.5 Centrifuge capable of maintaining > 2000 rpm for 10 minutes at ambient temperature.

6.6 Radiometer (optional) capable of monitoring the energy from a xenon source from 290 to 480 nm over time. Model PMA2100, Version 1.16, Solar Light Company, Inc., or equivalent. Consult the appropriate 3M SOP for instructions.

7.0 SUPPLIES AND MATERIALS

7.1 40 mL amber and clear glass VOA vials with screw caps with septa.

7.2 Crimp cap autovials-1.5 mL, caps, crimper, and decapper.

7.3 Adhesive-backed labels (return address size) for labeling quartz vials and autovials.

7.4 Disposable glass graduated pipettes, 1 mL to 10 mL.

7.5 Disposable glass Pasteur pipettes and rubber bulbs.

7.6 Glass beakers, various sizes.

7.7 Volumetric flasks, from 10 mL to 1000 mL.

7.8 Hamilton Gastight® syringes (precision ± 1% of the total volume), 5 µL to 1000 µL.

7.9 10 mL Bottle-top dispenser, Calibrex, Model # 511, or equivalent.

7.10 Adjustable repeater pipette, Wheaton Step-pette 411, or equivalent, equipped with the appropriate volumetric range pipette tips.

7.11 Ziploc® plastic bags, or equivalent.

8.0 REAGENTS AND STANDARDS

8.1 **Methanol (MeOH).** HPLC/SPEC/GC and/or purge and trap grade (EM Science, or equivalent.

8.2 **Acetonitrile (ACN).** HPLC/SPEC/GC and/or purge and trap grad from EM Science, or equivalent.

8.3 **Aqueous Matrix**, includes but is not limited to the following matrix types:

8.3.1 ASTM Type I water. Milli-Q® or equivalent, with a measured resistivity >18.0 MΩ-cm.

8.3.2 **0.01 M pH 7.0 Phosphate Buffer**. Example: Weigh 1.36 g KH_2PO_4 into a 2 L volumetric flask and dissolve into 1 L of Type I water. Add 600 mL of 0.1% NaOH. Adjust to pH 7.0 ± 0.1% with 0.1% NaOH or dilute H_2SO_4 and dilute to the mark with Type I water for a final conc. of 10 mM.

8.3.3 **Lake Surface water.** Collected from a known source, with known specifications for Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC).

8.3.4 **Sea water.** Collected from a known source, with known DOC and TOC specifications.

8.3.5 **Aqueous metal solutions and slurries (e.g. TiO_2, Fe_2O_3).** Example: Dilute 0.015 g of TiO_2 (Aldrich Chemical or equivalent) to 500 mL with Milli-Q® water.

8.3.6 **Aqueous solutions containing soil.** Example: Prepare samples containing 0.7g of characterized soil or sediment in 5 mL of Milli-Q® water.

8.4 Hydrogen Peroxide (H_2O_2). 30% aqueous solution from EM Science, or equivalent.

8.5 Potassium phosphate. Reagent grade from JT Baker or equivalent.

8.6 Stock Solutions

8.6.1 Stock solutions for the test analyte, target analytes, internal standard are prepared in an organic solvent (e.g. methanol, acetonitrile) at concentrations of approximately 10,000 µg/ml by weighting approximately 0.1g of the appropriate substance into a 10-mL volumetric flask and diluting to the mark with solvent. This solution is then diluted to make appropriate working solutions.

8.7 Test Analyte Solution:

8.7.1 Example for water soluble analyte(s):

Example: A 1 µg/mL test substance solution in the test matrix (Section 8.3) is prepared by diluting 0.050 mL of stock solution (Section 8.6.1) to 500 mL with test matrix. Aliquots (5 mL) of this solution will transferred to VOA vials for subsequent photolysis.

8.7.2 Example for poor water soluble analyte(s) or those with adsorption difficulties: Prepare a solution of the test substance in acetonitrile (Example: A 500 µg/mL test analyte solution is prepared by diluting 500 µl of stock solution (Section 8.6.1) into a 10 mL volumetric flask and diluting to mark with acetonitrile). Calculate the test analyte concentration such that the organic content in the test vial is no more than 1% of the total sample matrix volume.

Example: A 1 µg/mL test analyte in the test matrix (Section 8.3) is prepared by injecting 10 µL of a 500 µg/mL test substance stock (Section 8.6.1) into a VOA vial containing 5 mL of the test matrix.

**Acetonitrile is currently the preferred solvent to use when introducing the test substance to the test matrix because it does not interfere. Methanol is a radical scavenger, which can photooxidize during the exposure and decrease the indirect photolysis of the intended test substance. Evidence of this phenomenon (approximately 10% decrease in the concentrations of the final products) has been observed in a study here at 3M (EtFOSE-OH photolysis in pH 7 buffer, with and without presence of MeOH).*

8.8 Target Analyte(s) Spiking solution:

Example: A spike solution of test analyte and target analyte(s) (e.g. projected degradation products) in methanol or acetonitrile is prepared by diluting 500 µL of test analyte stock solution and 100 µL of target analyte(s) stock solution (Section 8.6.1) into 10 mL with MeOH. The final concentration is approximately 500 µg/mL test substance/ 100 µg/mL target analytes. Addition of 10 µL of this target analyte spiking solution into the 35-mL diluted sample volume will result in approximately 140 ng/ml and 30 ng/ml concentrations for the test analyte and target analyte(s), respectively.

**Pre-estimation of the degradation potential of the test analyte and subsequent degradation products is not always possible. If possible, an analytical pre-screening of representative samples should be performed for accurate spiking. General rule of thumb has been that the test analyte spike amount be*

approximately 25%- 50% of the initial concentration. The target analyte(s) spike amount has been 10-100 ng/ml, depending on expected levels under specific conditions.
More than one spike solution may be utilized to adequately represent the levels in the samples. Example: A test analyte that undergoes significant degradation during photolysis will require a lower spike concentration in the Exposed sample set due to less test analyte remaining. The Day 0 and Unexposed sample sets, which have not degraded, may require higher test analyte spike concentrations.

8.9 Dilution Solution containing Internal Standard:
The diluting solution shall contain internal standard at an area response level equivalent to approximately half the are response of the test analyte's high standard in the calibration curve. Enough dilution solution shall be prepared for use in all the study samples and in preparation of the calibration curve samples.
Example: Internal standard solution is prepared by diluting 100 µL of stock solution (Section 8.6.1) to 4.0 L with MeOH to a concentration of 250 ng/mL.

8.10 Quinine monohydrochloride dihydrate (QMD). 90% from Aldrich Chemical.

8.11 QMD solution: A 2% (w/v) solution of quinine monohydrochloride dihydrate solution is prepared by weighing approximately 2.0 g into a weigh boat, transferring to a 100 mL flask and diluting to volume with Milli-Q® water.

9.0 SAMPLE HANDLING

9.1 Record times of initial preparation, reference numbers of reagents used and the amounts, appropriate dates, times and initials on the photolysis sample preparation worksheet.. Record photolysis reactor used, radiometer (if applicable), computer for data collection, photolysis start and end on the sample preparation sheet and in the photolysis reactor log books. Record times, dates and initials of sample treatment post-photolysis, reference numbers of reagents used, and storage conditions.

9.2 Upon addition of the test substance solution, invert the 40 mL VOA sample vials (cap-side down) to prevent loss of any potential volatile target analytes during the rest of the procedure. This is particularly important for the GC/MS samples. GC/MS samples may only be turned upright immediately before being loaded onto the purge and trap autosampler. The LC/MS samples may be turned upright after the photolysis process has been completed. *The exception to this being the need to briefly turn the samples upright for H_2O_2 injection through the septa of the appropriate VOA sample vials at specified time intervals (See Section 12.6 and Section 12.11.7).*

9.3 The completed photolysis samples remain inverted and refrigerated at 1-5 °C prior to analysis by LC/MS or sample purge and trap GC/MS.

9.4 Sample preparation prior to LC/MS analysis requires the addition of 30 mL of diluting solvent containing internal standard to the 5-mL photolysis samples. This is to ensure complete recovery of the target analytes from the glass VOA vial surface and to dilute the samples into a working analytical range. Day 0 study samples stored at 1-5 °C during the time of photolytic exposure are removed and prepared for analysis at the same time as the exposed and unexposed samples.

10.0 QUALITY CONTROL

10.1 Refer to the definitions section for the quality control specified for each respective sample type.

11.0 CALIBRATION AND STANDARDIZATION

11.1 The compounds of interest must be characterized according to laboratory specifications.

11.2 All equipment used, such as the analytical balance, radiometer, etc. should be calibrated prior to use (daily, weekly, etc.) as specified in the standard operating procedure(s).

11.3 All samples analyzed will be run against a standard curve containing varying amounts of target analytes, and a fixed amount of internal standard or surrogate compound. Refer to the appropriate LC/MS and GC/MS methodologies for further analytical information.

12.0 PROCEDURE

12.1 Obtain the absorbance spectra of the test compound in aqueous solution using a UV-Visible Spectrophotometer (ETS-9-46.0).

12.1.1 Using a 10-cm quartz spectrophotometer cell, obtain a blank water absorbance reading over the range 290-800 nm to determine a background or baseline reading.

12.1.2 Aliquot a solution of water containing test substance, at a concentration less than half the solubility limit, into a 10 cm quartz spectrophotometer cell and obtain an absorbance reading over the range 290-800 nm. A positive absorbance may indicate the potential of the analyte to undergo direct photolysis. Non-absorbing analytes would be more likely to undergo indirect photolysis as the potential degradation pathway.

12.2 Obtain the appropriate number of clear and amber 40-mL glass vials with caps and cardboard boxes. Label the vial caps using a black permanent pen to distinctly identify samples. Paper labels will be applied post-hydrolysis as they don't stick in water.

12.3 Prepare appropriate sample preparation worksheets and create labels for each sample to affix to the 40 mL VOA vials and the autovials for analysis after photolysis. The labels should include the study number, sample number, test compound, matrix, exposure type (exposed/ unexposed/ Day 0), date and initials of the analyst.

12.4 Aliquot 5 mL of the following solutions into clear (for EXPOSED samples) and amber (for UNEXPOSED and DAY 0 samples) 40 mL glass VOA vials:

12.4.1 Matrix with test substance (sample reps 1,2,3, and sample spike).

12.4.2 Matrix without test substance (matrix blank and matrix blank spike).

12.4.3 Control matrix with test substance (control sample and control spike).

12.4.4 Control matrix without test substance (control blank and control blank spike).

(When appropriate, test substance may be added after 5mL aliquots of matrix have been added to the vials. See Section 8.7)

12.5 All exposed, unexposed, and day 0 samples will contain sample sets with and without peroxide and prepared for LC/MS and GC/MS analyses according to the following table:

Sample Treatment/Type	# of Samples	# of Spikes
Matrix with test substance	6 +H_2O_2 (3LC/MS,3GC/MS) 6 -H_2O_2 (3LC/MS ,3GC/MS)	2 +H_2O_2 (1LC/MS,1GC/MS) 2 -H_2O_2 (1LC/MS,1GC/MS)
Matrix without test substance	2 +H_2O_2 (1LC/MS,1GC/MS) 2 –H_2O_2 (11LC/MS,1GC/MS)	2 +H_2O_2 (1LC/MS,1GC/MS) 2 -H_2O_2 (1LC/MS,1GC/MS)
Control matrix with test substance	2 +H_2O_2 (1LC/MS,1GC/MS) 2 –H_2O_2 (11LC/MS,1GC/MS)	2 +H_2O_2 (1LC/MS,1GC/MS) 2 –H_2O_2 (11LC/MS,1GC/MS)
Control matrix without test substance	2 +H_2O_2 (1LC/MS,1GC/MS) 2 –H_2O_2 (11LC/MS,1GC/MS)	2 +H_2O_2 (1LC/MS,1GC/MS) 2 –H_2O_2 (11LC/MS,1GC/MS)
EXPOSED, UNEXPOSED, & DAY 0	24 x 3 per exp type = 72	16 x 3 = 48
Total Samples per compound per study = 120 (60 for LC/MS, 60 for GC/MS)		

12.6 Separate the vials into three boxes labeled "Day 0," "Exposed," and "Unexposed." Initial addition of peroxide (Section 8.4) is done at this time by removing the cap and injecting the appropriate amount (e.g. 10 – 50 µL) into the vial. (Subsequent additions of peroxide shall be injected through the septa of the VOA vials.)

12.7 **For use of quinine actinometer (Optional):** Prepare a batch of quinine irradiation control samples by aliquoting 5 mL of the 2% aqueous solution (Section 8.8) into the appropriate number of clear and amber 40 mL I-CHEM vials. Prepare one clear and one amber vial per reactor, per day of exposure. Store the vials at 1-5 °C and protected from light prior to use. Place one clear vial in the reactor per day, while removing exposed quinine controls. Exposed quinine controls need to be wrapped in foil upon removal to protect from further exposure. Store at 1–5 °C prior to measuring the absorbance via UV-Vis Spectrophotometer. The absorbance measurement should be performed as soon as possible, as the absorbance increase rate after light source removal may be 20% of the rate of when light is present. (Reference 18.5).

12.8 Place all the "Day 0" samples immediately in a cooler at 1-5 °C or freeze at a continuos temperature of less than 0 °C, inverted and protected from light.

12.9 Place "Unexposed" sample vials (amber) into Ziploc® bags separated and labeled as "with peroxide" and " without peroxide", respectively. Place the bags in the bottom of the water bath, under the photoreactor tray that holds the exposed samples. The "unexposed" samples will remain immersed in the 23-26 °C water bath under the exposed samples for the duration of the exposure. Include one quinine control sample in an amber vial with the unexposed sample set.

13.0 PHOTOREACTOR SET UP

13.1 Set the irradiation intensity at the desired output. For most experimental conditions, an intensity of 261 W/m^2 is chosen because it yields the equivalent average optimum natural daylight radiation for 300-400 nm at known latitude. (see the table below):

	Approximate Integrated and Individual Irradiances in W/m^2				
Irradiance Source	250-300 nm	300-400 nm	400-800 nm	340 nm	420 nm
Average Optimum **Natural Daylight**[1]	0.0	27.8	259.0	0.30	0.67
Atlas Photoreactor with integrated irradiance output of 261 W/m^2 300-800 nm using the IR Reflecting and 290 cut-on filters	0.08	27.8	234.36	0.24	0.71

[1]*Measured, Miami, Florida (18.3)*

13.2 For all "Exposed" samples, invert the vials cap-side down and vertical in the photoreactor tray holders to a depth that ensures that half the VOA vial is submersed in the 23-26 °C water bath. Include one quinine control sample (Section 12.8) in a clear vial with the exposed sample set.

13.3 Close the door to the photoreactor and turn the door knob completely so the sensor detects that the door is completely shut.

13.4 Turn on the water cooler bath, ensure that it is set between 23-26 °C.

13.5 Turn on the photoreactor pump and the power to the reactor.

13.6 Set the irradiation program using the following parameters in the table below:

Photoreactor conditions

Parameter	**Setting**
Program #, # of Phases	1,1
Flowing Water ("FW")	ON
Irradiation intensity	Example: 261 watts/m^2
Duration of exposure	Example: 8 hours

13.7 After entering the appropriate parameters within the menu, select program #1 to run and start the irradiation program. Upon lamp ignition, the water bath begins to fill and circulate. Visually check for both lamp and water bath activation as an indication of proper initiation of the photoreactor. When removing samples during the exposure period, select "stop" from the photoreactor keypad. Open the door and carefully remove the sample rack. ***Caution: The walls of the chamber are hot and sensitive to scratching.*** To restart the program, close the door, ensure that the door knob is turned all the way in and press "start" on the reactor module. Visually inspect for proper lamp ignition and water bath circulation.

13.8 At the specified time, spike appropriately labeled sample types with a known volume (e.g. 10-50 µL) of 30% H_2O_2 solution (Section 8.4) and swirl to ensure adequate mixing. Maintain the inverted position of samples removed for spiking pre- and post- the actual peroxide injection. Return samples to their designated locations (bottom of reactor pan

for the unexposed samples, reactor tray holder for the exposed samples, or the cooler for the Day 0 samples). ***Note: Don't forget to add peroxide to appropriate Day 0 samples!***

13.9 Remove the exposed quinine control sample from the reactor tray and visually confirm a color change as an indicator of photoreactor performance. The solution should be a gray/brown color after irradiation. Record the total time exposure of the sample, wrap the sample in foil to protect from light and analyze the quinine sample. Place a new quinine solution vial into the photoreactor tray with the exposed samples. ***Note: Quinine samples do NOT receive peroxide.***

13.10 Record the chamber temperature daily on the sample prep sheets.

13.11 Upon completion of the photolytic exposure, samples are removed, labeled with adhesive-backed labels and the study sets (Exposed, Unexposed and Day 0) organized for LC/MS or GC/MS analysis. If subsequent analysis can not be performed immediately, store samples in a cooler at 1-5 °C.

13.12 Pertinent information regarding start and stop times of photoreactor exposure study, water bath and chamber temperatures, addition of peroxide, and an explanation of unexpected occurrences shall be documented on the sample preparation worksheets, with appropriate dates, times and initials.

14.0 SAMPLE PREPARATION FOR ANALYSIS.

14.1 LC/MS sample extraction and prep.

14.1.1 Dilute all 5 mL samples by a factor of 1:7 v/v by adding 30 mL of an appropriate analytical solvent containing internal standard (Section 8.6.2) to all vials.

14.1.2 Add spike solution (Section 8.6) containing the target analytes to the appropriate samples.

14.1.3 Ensure the sample vials are inverted several times to ensure adequate mixing.

14.1.4 If samples appear cloudy, and/or the sample matrix appears unclear, it may be necessary to centrifuge the samples, at an appropriate speed and duration (e.g. 2000 rpm for 10 minutes), until no noticeable particulate matter is suspended in the sample.

14.1.5 Aliquot approximately 1 mL into autovials and tightly cap.

14.2 GC/MS sample preparation.

14.2.1 Set up autosampler and concentrator methods. If samples have been kept in cold storage, bring samples to room temperature (approximately 23-26 °C).

14.2.2 Spike vials through the septa and place in the autosampler.

15.0 DATA ANALYSIS AND CALCULATIONS

15.1 The amount of target analytes in the sample will be quantified against a standard curve regression.

15.2 Means will be calculated by adding the individual entities and dividing the resultant sum by the number of individual entities.

15.3 Standard deviations will be calculated using either Microsoft Excel® or Microsoft Access® to calculate standard deviation. The built in function contains the following equation which is based on the individual entities (n) being less than 30:

$$\sqrt{\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$$

15.4 Sample precision will be reported as % relative standard deviation (% RSD). Sample % RSD will be calculated using the following equation:

$$A/B \times 100 = \text{Sample \% RSD}$$

where: A= standard deviation of averaged samples
B= average of samples

16.0 METHOD PERFORMANCE

16.1 Refer to the definitions section for the method performance specifications/criteria for each respective sample type.

17.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

17.1 Dispose of sample waste by placing in high or low BTU containers as appropriate. Use broken glass containers to dispose of glass pipettes.

18.0 RECORDS

18.1 Fill out the photolysis sample preparation worksheet documents completely, making sure to include all initials and dates. Store photolysis sample preparation worksheets in the raw data file.

18.2 Enter all standard, stock, solutions, etc. preparation information in the proper preparation logbook(s). Make a photocopy of the logbook pages used, and include the copy in the raw data file. Photocopied logbook pages will be included in the final data packet.

18.3 Archive electronic data to compact disc media.

19.0 ATTACHMENTS

19.1 Attachment A: Example Photolysis Prep sheet.

20.0 REFERENCES

20.1 Crosby, Helz, and Zepp. Aquatic Surface Photochemistry. p 480

20.2 Interpersonal conversation with Carrie O'Connor, Optical Systems Engineer, Atlas Electric Devices.

20.3 "Suntest CPS/CPS+ Spectral Irradiance Distribution," table distributed by Atlas Electric Devices Company, sent via fax by Richard Sherwin, Sales Representative, 26 July, 2000.

20.4 "Atlas Xenon Filter Combination and Sunlight Measurements," information generated by Atlas Electric Devices Company sent via fax by Richard Sherwin, Sales Representative, 26 July, 2000.

20.5 Bergstrom, David H., Thomas C. Kester, and Shangdong Zhan. "Quinine Chemical Actinometry Studies Under Two Light Sources Specified by the ICH Guideline on Photostability Testing."

21.0 AFFECTED DOCUMENTS

21.1 None

22.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

Attachment A – Photolysis Sample Prep Sheet

Fluorochemical Degradation (Photolysis) Analysis Sample Prep Sheet

Test Analyte: _____
Project/Lab Request Number _____
Exposure Type: _____
Nominal Expos _____
Analysis: LC/MS

**Following initial sample prep, all samples will be placed cap-side down and vertical.*
Following photolysis, Day 0 samples will be pulled and extracted with Exposed and Unexposed samples

Sample Matrix: _____
Control Matrix: _____

		Sample Matrix	Test Analyte	Peroxide	Internal	Spike Solution	Comments:
	Volume:						
	Date:						
	Time:						
	Initials:						
Sample No.	Description / Sample Type	Solution I.D.	Solution I.D.	Solution I.D.	Solution I.D.	Solution I.D.	Comments:
	Rep 1 / Day 0						
	Rep 2 / Day 0						
	Rep 3 / Day 0						
	Spike / Day 0						
	Matrix Blank / Day 0						
	Matrix Blank Spike / Day 0						
	Control Rep 1 / Day 0						
	Control Spike / Day 0						
	Control Blank / Day 0						
	Control Blank Spike / Day 0						
	Rep 1 / Exposed						
	Rep 2 / Exposed						
	Rep 3 / Exposed						
	Spike / Exposed						
	Matrix Blank / Exposed						
	Matrix Blank Spike / Exposed						
	Control Rep 1 / Exposed						
	Control Spike / Exposed						
	Control Blank / Exposed						
	Control Blank Spike / Exposed						
	Rep 1 / Unexposed						
	Rep 2 / Unexposed						
	Rep 3 / Unexposed						
	Spike / Unexposed						
	Matrix Blank / Unexposed						
	Matrix Blank Spike / Unexposed						
	Control Rep 1 / Unexposed						
	Control Spike / Unexposed						
	Control Blank / Unexposed						
	Control Blank Spike / Unexposed						
	Component(s) and Solution Concentration						

General Notes:
Check mark - Indicates the solution added.
n/a = not applicable
[illegible] as require different solution ID.
[illegible] as require no addition of solution

Photolysis Reactor I.D.:			Freezer/Refriferator Storage I.D.:		
Start Date:	Time:	Initials	Start Date:	Time:	Initials
Stop Date:	Time:	Initials	Stop Date:	Time:	Initials

Total Exposure: _____ days _____ hours _____ min

Comments: _____

3M ENVIRONMENTAL LABORATORY

EQUIPMENT PROCEDURE

OPERATION AND MAINTENANCE OF THE SUNLIGHT EXPOSURE SYSTEM, IMMERSION UNIT, AND RECIRCULATING WATER CHILLER SYSTEM

Procedure Number: ETS-9-44.0 **Adoption Date:** 10/20/00

Exact Copy of Original

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Initial Date

Revision Effective Date:

Approved by:

Laboratory Management 10/20/00 Date

Team Leader Oct 17, 00 Date

1.0 SCOPE AND APPLICATION

1.1 This equipment procedure describes the regular operation and maintenance of the Atlas SUNTEST® Sunlight Exposure System equipped with an immersion unit and recirculating water chiller.

2.0 DEFINITIONS

2.1 **Photon energy:** $U = hv = hc/\lambda$ where h is Planck's constant, c is the speed of light, and v and λ are the frequency and wavelength of light. Therefore, the energy of a photon, U, is inversely proportionate to the wavelength.

2.2 **Irradiance:** The energy output ("U" in the above equation for energy of a photon) in Watts/m^2 specific to a wavelength or wavelength range. The irradiance output specific to the types of Atlas wavelength filters available (Reference 14.9) should be used as a guide to calculating the global irradiance (in units of W/(m^2nm) needed to give a specific energy over a desired wavelength range.

3.0 DESCRIPTION

3.1 The Atlas SUNTEST® Sunlight Exposure System (CPS+ or XLS+) produces visible and ultraviolet light (250-765 W/m^2). Light produced is filtered with a filter or combination of filters to allow specific wavelength ranges. Samples are exposed to the light in a reflecting chamber. An immersion unit with water recirculation through a chiller provides a cooled, constant sample temperature.

4.0 IDENTIFICATION

4.1 Atlas SUNTEST® XLS+, equipped with a xenon arclamp, lamp filter(s) available from Atlas to allow specific irradiance ranges, and immersion unit.

4.2 Atlas SUNTEST® CPS+, equipped with a xenon arclamp, lamp filter(s) available from Atlas to allow specific irradiance ranges, and immersion unit.

4.3 Neslab CFT-33 Refrigerated recirculator or equivalent

5.0 WARNINGS AND CAUTIONS

5.1 Health and Safety Warnings:

- 5.1.1 Wear appropriate laboratory safety personal protective equipment.
- 5.1.2 The xenon lamp emits ultraviolet light which can cause burns to the skin and permanent damage to the eyes. Never attempt to operate the unit with the test chamber door open.
- 5.1.3 When filling the sample immersion unit with water, always shut off all power to the SUNTEST® device and the immersion unit to prevent electrical shock.

5.2 **Cautions:**

- 5.2.1 Handle optical parts carefully; fingerprints on the lamp, filter or quartz dish can result in altered spectral output or early lamp failure.
- 5.2.2 The reflective coating of the test chamber walls is sensitive to scratches. Do not use any abrasives or harsh cleaning agents that may cause scratches and non-uniform illumination of the test chamber.

5.2.3 Keep SUNTEST® unit clear of obstructions that would block vents; overheating may cause blown fuses, shortened lamp life or other damage.

5.2.4 After beginning the experiment, always make sure that the sample vials are sufficiently submerged. Excessive heat may affect the results of the experiment.

5.2.5 Manually drain the immersion tank on the XLS+ models after stopping the run; otherwise, the water will overflow.

6.0 SPECIAL INSTRUCTIONS

6.1 None.

7.0 RESPONSIBILITY

7.1 The analytical group of personnel who routinely operates the equipment is collectively responsible for the instrument operation as described in this document. The person responsible for maintenance and calibration (and an alternate) will be identified in the front of the equipment logbook.

8.0 SUPPLIES AND MATERIALS

8.1 Xenon lamp for XLS+, Atlas PN 56077798

8.2 Xenon lamp for CPS+, Atlas PN 56001794

8.3 Hand-tools as required

8.4 Kim-Wipes™

8.5 Optional radiation filter(s) for lamp available from Atlas:

Filter/ Atlas Part Number	Properties
Quartz Dish w/ IR reflective coating, PN 56052388	IR reflective coating (supplied standard with unit)
Quartz Dish, PN 56052373	Uncoated (to allow higher black standard temperatures)
UV Special Suprax® Filter, PN 56052371	Cut-on at 290 nm, simulates outdoor solar radiation.
Window Glass Filter, PN 56052372	Cut-on at 310 nm, simulates exposure behind 3 mm (0.118 in.) window glass.
Window Glass Solar ID 65 Filter, PN 56077769	Cut-on at 320 nm, simulates exposure behind 6 mm (0.236 in.) window glass. (Must be used with Window Glass Filter above.)
Solar Standard Filter, PN 56077759	Cut-on at 290 nm, simulates outdoor solar radiation at optimal UV intensity.

9.0 CLEANING PROCEDURES

All routine and non-routine cleaning procedures will be performed by person(s) designated in the front of the instrument logbook; see Section 12).

9.1 Routine cleaning

9.1.1 Clean the inlet air filters at the back of the SUNTEST® unit every 6 months with a mild soap solution. Rinse in clean water. When more severe contamination is present, vacuum the filters or replace them.

9.1.2 Clean the reflector in the test chamber when it is dirty, using a soft cloth and mild soap solution. DO NOT use any abrasive cleaning materials or the reflector may be permanently damaged and irradiance uniformity will be altered.

9.1.3 Clean and/or flush the water tank and water lines on the immersion unit monthly to prevent build up of residue in the circulating water system.

10.0 MAINTENANCE PROCEDURES

10.1 Routine maintenance will be performed by the person(s) designated in the front of the equipment log (see Section 12):

10.1.1 Replace the xenon lamp after 1500 hours or when the required irradiance level cannot be achieved (e.g. error message reads "E MAX Power reached; CHANGE XENON LAMP") Refer to the SUNTEST® instruction manual for details on how to replace the lamp.

10.1.2 If the temperature near the lamp becomes too high, the fuse blows to interrupt power and save the lamp (indicated by the error message "DOOR OPEN or TEMPERATURE FUSE"). Refer to the SUNTEST® instruction manual for details on how to replace the fuse.

10.1.3 Record routine maintenance in the equipment log (see Section 12).

10.2 Non-routine maintenance will be performed by the person(s) designated in the front of the equipment log (see Section 12):

10.2.1 If the equipment fails to operate, refer to the equipment manual for further instructions, if necessary. Contact the Team Leader for instructions if the equipment cannot be made operational.

10.2.2 If an abnormal operating situation occurs or if calibration verification fails, contact the responsible individual identified in the equipment log. Label the equipment as "out of service" if it cannot be immediately repaired.

10.2.3 Record non-routine maintenance in the equipment log (see Section 12).

11.0 INSTRUMENT CALIBRATION

11.1 The photoreactor is set to maintain a specified integrated energy output. The amount of energy output from the lamp may be monitored with the use of a radiometer. The radiometer system will provide and record instantaneous energy output. Refer to ETS-9-50.0 Operation and Maintenance of Radiometer and Detector.

11.2 Calibration of SUNTEST® systems will be performed two times each year by Atlas Electric Devices Company.

12.0 OPERATING PROCEDURES

12.1 For more detailed operating instructions refer to the equipment operating manuals.

12.2 Immersion Unit

12.2.1 To begin operation, fill the tank with water until the level indicator is up to the full mark.

12.2.2 Turn the power on.

12.3 Chiller

12.3.1 Turn the power on. Set water temperature knob to desired set point. Allow temperature to equilibrate before igniting the SUNTEST® lamps.

12.4 SUNTEST® XLS+ or SUNTEST® CPS+ unit set-up

12.4.1 Select the desired wavelength filter from the parts listed under Section 8.4 to achieve the proper irradiation specified in the program, and program the photoreactor with the filter type information:

With the photoreactor menu in the "Program" mode, select the appropriate filter combination type:

Optical Filter System Designations
A: Coated quartz glass only
B: Coated quartz glass with UV special glass
C: Coated quartz glass with window glass
D: Uncoated quartz glass only
E: Uncoated quartz glass with UV special glass
F: Uncoated quartz glass with window glass

12.4.2 Selection/determination of energy output (W/m^2)

12.4.2.1 Irradiance control and display is between 250-765 W/m^2 (nominally 300-800 nm). The irradiance is determined by the settings of the test program [including type of filter(s) used]. The selectable range is from 250 W/m^2 to 765 W/m^2 (page 12, XLS+ Instruction manual). The total (integrated) energy output (300-800 nm) is directly dependent on the type of lamp filter(s) used. E.g. if the filter has a narrow range such as a cut-on at 400 nm, all irradiance energy coming from wavelengths <400 nm will not reach the samples, and the total integrated irradiance will be less than if the filter's cut-on was at, for example, 290 nm.

12.4.2.2 Once the proper filter(s) is/are designated, the photoreactor will base the energy output on what type of wavelengths are being allowed to pass through the filter system to reach the samples. To calculate the energy output to program into the system, refer to References 14.7, 14.8 and 14.9 as guides to calculate the desired spectral irradiance. Reference 14.7 may be used to calculate the programmed global irradiance necessary to achieve desired irradiances at specific wavelengths or wavelength ranges. Reference 14.8 may be used to reference sunlight measurements and to correlate natural sunlight to the Atlas Suntest® photoreactors. Reference 14.9 is a useful reference for determining irradiances at a specific

wavelength or a wavelength range using specific filter combinations at specified global irradiances of 250, 500, and 765 W/(m^2nm).

12.5 Photoreactor Analysis set up

12.5.1 Place VOA (volatile organic analysis) vials containing samples (see the appropriate analytical method) into the test chamber. Sample vials to be exposed must be cap side down to allow light to enter the vial. Tighten caps securely to prevent leakage. Secure the vials in the chamber to prevent floating once the water begins to circulate.

12.5.2 Close the chamber door and turn the power on.

12.5.3 From the initial LCD display, use the arrow keys to select Program. Press "Enter".

12.5.4 If programming a new method is necessary, use the arrow key to select Programming. Press "Enter".

12.5.5 Input program number, number of phases, desired irradiance, immersion function, phase time and switch off criteria. Each entry is followed by the "Enter" key.

12.5.6 To start the program, select "Program Start" and press the "Enter" key.

12.5.7 Press "Escape" for the next screens if the filter has not been changed and no printout is desired. Input program number and press "Start"

12.5.8 Program will begin with lamp ignition. Note: Due to the modified sample chamber in the SUNTEST® XLS+ models, the water initially present in the immersion tank is not sufficient to fill the sample chamber once a program has started. Refill the immersion unit as the water level drops below the fill line. Once a program has finished, drain the immersion tank so that it does not overflow when water from the sample chamber drains back down into the immersion unit. Failure to do so may result in remote flooding.

12.5.9 To interrupt operation (e.g. to add peroxide reagent)Press "Stop". If it is necessary to turn the power off (to exchange the lamp, for example) wait until the fan turns off in 1-3 minutes before turning power switch to "Off" and unplugging the power cord. When ready to continue operation, turn power "On".

12.5.10 To resume operation, press "Start". The program will continue at the point of interruption.

12.5.11 To read parameters during the program run, scroll through the parameters of the running program by using the arrow keys. This is helpful to see how many more hours are remaining in the running program.

12.5.12 The SUNTEST® will shut off automatically when the switch-off criteria are reached. To display the total time and irradiance, press "Enter". Record exposure time in instrument run log. Then turn power "Off".

12.5.13 To manually stop the program, press "Stop". Wait until lamp is cooled, then press "Escape". Power can then be turned "Off".

13.0 RECORDS

13.1 Instrument logbooks

13.1.1 Equipment Log: The person(s) designated at the front of the equipment log will record all cleaning and maintenance activities in the appropriate log for each SUNTEST® system. Records for routine maintenance of equipment must include the dates of the operation, whether the operations followed the SOP, and the initials of the person performing the operation. Records for non-routine repairs performed as a result of instrument failure or malfunction must include the nature of the defect, how and when the defect was discovered, any remedial action taken in response to the defect, and the date and initials of the person performing the maintenance. Maintenance by outside contractors should include their name and company affiliation.

13.1.2 Run Log: Record each experiment in the appropriate instrument logbook. Enter the operators initials, time and date of exposure, lamp intensity and water temperature as the samples are placed in the chamber. When samples are finished, record the time and date when samples came out, the ending chamber temperature and the actual hours of exposure. All entries made in the run log should be initialed and dated.

13.1.3 SUNTEST® Data Output Log: XENOVIEW® 2.2 Storage Software will receive and record the measurement data transferred from the SUNTEST® system to a computer or printer, while a program is in progress. The measurement data recorded includes: number of phases, phase time, chamber temperature, radiant exposure, irradiance, running time, date and time data is recorded. Refer to XENOVIEW® software instruction manual for details on how to operate software. Any printouts of program or other data should be initialed and dated prior to adding to the study file.

13.2 Identification records for each system include equipment ID, manufacturer, model number, and serial number of each individual component. In addition, if components are removed or added, the above information must be written in the logbook including the date the change was made and initials of the analyst completing the change.

14.0 REFERENCES

14.1 SUNTEST® XLS/XLS+ Instruction Manual, Doc. No. 20-8036-00 Rev. 0 12/98 Atlas Electric Devices Company.

14.2 SUNTEST® CPS/CPS+ Operating Manual, 6/97 Atlas Company.

14.3 SUNTEST® XLS+ Immersion Device Operating Manual, 2/99 Atlas Company.

14.4 SUNTEST® CPS+/XLS+ Software Documentation 1.4 Atlas Company.

14.5 XENOVIEW® 2.2 Storage Software Operating Instructions.

14.6 ETS-9-50.0, Operation and Maintenance of Radiometer and Detector.

14.7 "SUNTEST®Irradiance in W/m^2*nm". Tables furnished by Atlas Company.

14.8 "Atlas Xenon Filter Combination". Table furnished by Atlas Company.

14.9 "SUNTEST® CPS/CPS+ Spectral Irradiance Distribution". Table furnished by Atlas Company.

15.0 AFFECTED DOCUMENTS

15.1 None.

16.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

3M ENVIRONMENTAL LABORATORY

ANALYSIS OF FLUOROCHEMICALS BY ARCHON PURGE AND TRAP AUTOSAMPLER, TEKMAR PURGE AND TRAP CONCENTRATOR AND AGILENT GAS CHROMATOGRAPH/MASS SPECTROMETER

Procedure Number: ETS-8-182.0 **Adoption Date:** 10/20/00

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Revision Date:

Approved by:

Laboratory Manager 10/20/00 Date

Team Leader Oct 20, 00 Date

1.0 SCOPE AND APPLICATION

1.1 Scope. This method is used for the analysis of selected hydrolysis and photolysis samples for the presence of degradation products such as olefins and hydrides using gas chromatography/mass spectrometry in a full scan mode. An Archon autosampler and Tekmar Purge and Trap concentrator (or an equivalent system) is coupled to a GC for purging analytes from the liquid matrix and concentrating them on the trap column before injecting on to the GC.

1.2 Applicable compounds. Compounds that may be analyzed by this method are listed below. Other fluorochemicals may be detected by monitoring mass spectra and running library comparison. Compounds that are detected but do not have appropriate standards, will be quantified relative to structurally similar standard compounds listed below.

- **1.2.1** 1H-perfluoroethane (1H-pfC2)
- **1.2.2** Perfluro-2-butene (pfC4-2ene)
- **1.2.3** 1H-perfluropropane (1H-pfC3)
- **1.2.4** 1H-perfluorobutane (1H-pfC4)
- **1.2.5** Perfluoro-2-heptene (pfC7-2ene)
- **1.2.6** Perfluoro-1-heptene (pfC7-1ene)
- **1.2.7** 1H-perfluorohexane (1H-pfC6)
- **1.2.8** Perfluoro-2-octene (pfC8-2ene)
- **1.2.9** 1H-perfluoroheptane (1H-pfC7)
- **1.2.10** 2H-perfluorooctane (2H-pfC8)
- **1.2.11** 1H-perfluorooctane (1H-pfC8)

1.3 Instrument Surrogate compounds. Added at the time of analysis and used to monitor performance of purge and trap autosampler and concentrator.

- **1.3.1** Dibromofluoromethane
- **1.3.2** Toluene-d8
- **1.3.3** 4-Bromofluorobenzene
- **1.3.4** Pentafluorobenzene
- **1.3.5** 1,4-Difluorobenzene
- **1.3.6** Chlorobenzene-d5
- **1.3.7** 1,4-Dichlorobenzene-d4

1.4 Sample Surrogate compounds. May be added at the time of sample preparation.

- **1.4.1** Perfluorocyclohexane

2.0 SUMMARY OF METHOD

2.1 A dynamic purge and trap system (autosampler and concentrator) is coupled to a temperature programmed GC for analyte separation and subsequent mass spectrometer detection and quanitation. The liquid sample is purged for 20 min. in the sample vial, and the volatile components are swept onto a chemical trap in the concentrator. In the subsequent desorption mode, gas flows in opposite direction and temperature of the chemical trap increases to 250 °C. The trapped analytes are transferred onto the GC column for GC/MS separation, detection, and quanitation. Through this process, a high volume of sample is injected and most of the non-volatile matrix components stay in the sample vial, allowing low level detection of fluorochemicals.

3.0 DEFINITIONS

3.1 **Calibration Standard.** A dilution of various amounts of a stock, intermediate or purchased standard to achieve standard solutions in a concentration range of interest.

3.2 **Calibration Curve.** The graphical relationship between known values, such as concentration of a series of calibration standards and their instrumental response.

3.3 **External Standard Quantification.** Process of establishing the concentration of a target analyte by plotting the theoretical amount (in units of ng/mL or µg/mL, etc.) versus the response of the target analyte(s) on column. The resultant curve(s) shall be used to determine unknown concentrations by comparing the area response of target analyte(s) to the area response and corresponding analyte amount on the appropriate analyte's calibration curve.

3.4 **Coefficient of Determination (r^2).** The square of the correlation coefficient. It is the proportion of the variation in the dependent variable that is accounted for by the independent variable.

3.5 **Instrument Surrogate.** An organic compound similar to the target analyte(s) in behavior in the analytical process, but is not normally found in the sample(s). A surrogate may be added to sample vial during instrument analysis.

3.6 **Sample Surrogate.** An organic compound similar to the target analyte(s) in chemical composition and behavior in the analytical process, but is not normally found in the sample(s). A surrogate may be added to sample triplicates and matrix spike samples along with the test analyte (pre-photolysis).

3.7 **Continuing Calibration Verification (CCV).** Standards analyzed during an analytical run to verify the continued accuracy of the calibration curve. This solution may or may not be prepared from a different source or lot number than the calibration curve standards.

3.8 **Solvent Blank.** A sample of analyte-free medium that is not taken through the sample preparation process. This blank is used to evaluate instrument contamination.

3.9 **Blank.** For photolysis studies, there are multiple blanks to adequately represent the variables of the study (Exposed, Unexposed and Day 0 samples with/without peroxide addition). The blank is carried through the sample preparation, photolytic and analytical procedures to monitor for contamination during any step. It is also used to establish a chromatographic baseline/background and monitor for analytical interference or suppression of target analyte(s) from the matrix.

3.9.1 **Matrix Blank:** A sample of analyte-free matrix (buffered water, lake water, etc.) to which all reagents are added in the same volumes or proportions as used in sample processing. It is used to document the test system without test analyte.

3.9.2 **Control Blank:** A sample of analyte-free matrix (Milli-Q water) to which all reagents are added in the same volumes or proportions as used in sample processing. It is used to control the test matrix and monitor matrix specific

background levels, interferences or suppression of target analyte(s) from the matrix.

3.10 **Limit of Quantitation (LOQ).** The lowest concentration that can be reliably measured within specified limits of accuracy during routine laboratory operating conditions. The LOQ is generally 5 to 10 times the minimum concentration with a 99% confidence limit that the concentration is greater than zero. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes, the LOQ is selected as the lowest non-zero standard in the calibration curve that is greater than 4 times the level of the matrix blank.

3.11 **Sample Triplicates.** Three samples taken from and representative of the same sample source. These are prepared separately and carried through all steps of the exposure, extraction and analytical procedures in an identical manner. There are multiple sets of triplicate samples to adequately represent the photolytic variables of the study (Exposed, Unexposed and Day 0 with/without peroxide addition). Triplicate samples are used to assess variance of the photolytic method, including sample preparation, photolysis exposure, and analysis.

3.12 **Relative Standard Deviation (RSD).** A measure of precision defined as the standard deviation of three or more values divided by the average of the values and multiplied by 100. (Also reported as Coefficient of Variation (CV)).

3.13 **Analytical Spike.** Prepared by adding a known mass of target analyte(s) to a specified amount of a sample or control matrix prior to analysis. This assumes that an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the matrix on method recovery efficiency.

3.14 **Accuracy.** The closeness of agreement between an experimentally determined value and an accepted reference value. When applied to a set of observed values, accuracy is a combination of a random (precision) and a common systematic (bias) component. For purposes of the study, the acceptance criterion is 75% to 125% of the nominal value.

3.15 **Geometric Mean of the calibration curve:** The square root of the product of the high standard concentration and the low calibration curve standard. When preparing calibration curve standards, the number of calibration standards below the geometric mean shall equal the number of calibration standards above the geometric mean. Having equal distribution of calibration standards above and below the geometric mean when analyzing and reprocessing data, effectively weights the curve such that both the high and low ends of the curve are given equivalent significance.

4.0 WARNINGS AND CAUTIONS

4.1 Health and Safety Warnings:

4.1.1 The operator must be familiar with the purge and trap autosampler/concentrator/GC/MS system and associated hazards, such as high temperature, effluent venting, solvent use, and low-pressure vacuum system. See instrument manuals

4.1.2 All exhaust vents, including the GC oven vent, Tekmar concentrator purge vent, split vent and mass spectrometer pump exhaust must be connected to the laboratory vent system to keep potentially hazardous effluent from mixing with laboratory air.

4.2 Cautions:

4.2.1 It is recommended that a grounded antistatic wrist strap be worn while disconnecting all wires, contacts, or cables which are connected to printed circuit boards within the Archon autosampler, Tekmar concentrator or MS analyzer.

4.2.2 To prevent the breakage of the Standard Vial on the Archon autosampler, do not use any tool and do not overtighten the thumbnut.

5.0 INTERFERENCE

5.1 Methanol, water and other co-extracted matrix components could interfere with detection decreasing sensitivity.

6.0 EQUIPMENT

6.1 System: "Rufus", or equivalent:

6.1.1 Autosampler: Varian, Archon

6.1.2 Concentrator: LSC2000, Tekmar

6.1.3 GC: 6890, Agilent

6.1.4 MS: 5973N, Agilent

6.1.5 Column, GS-GASPRO 60m x 0.23mm, J&W

7.0 SUPPLIES AND MATERIALS

7.1 Helium, ultra-high-purity

7.2 40ml VOA vials, e.g. I-Chem, S236-0040

8.0 REAGENTS AND STANDARD

8.1 Methanol, Purge and Trap grade or equivalent

8.2 **Standards**. Typically a minimum of five calibration standards, ranging from 1 ng/ml to 20 ng/ml are prepared. This concentration range should bracket the concentration of samples and matrix spikes; if the analyte concentration exceeds this range, then the calibration range should be increased.

8.3 **Instrument Surrogates**. Used only to monitor performance of purge and trap autosampler and concentrator and not for quantitation.

8.4 **Sample Surrogates**. May be used to monitor sample preparation, photolytic exposure and analytical performance.

9.0 SAMPLE HANDLING

9.1 Store standards and samples in the refrigerator at $4^{\circ}C \pm 3^{\circ}C$ until analysis time.

9.2 For the analysis, pull samples and standards out of the freezer and bring them to room temperature.

10.0 QUALITY CONTROL

10.1 **Calibration Standards.** Calibration standards (Section 11) used to generate a calibration curve. The number of calibration standards and the concentration levels should be sufficient to encompass the expected concentrations of the study samples. In general, a minimum of five calibration standards is required for fit of linear regression.

10.2 **Continuing Calibration Verification (CCV).** Analyze a mid-range calibration standard after a maximum of every fifteen samples.

10.3 **Solvent blank.** Solvent blanks are run before and after every calibration curve, CCV, matrix and control blank (see 3.9.2), and after batches of no more than 30 injections. Acceptable values for the blanks are values below 25% of the limit of quantitation (LOQ) of the instrument. If analyte carryover is a problem, use back-to-back solvent blanks.

10.4 **Sample Triplicates.** Prepare and analyze all samples in triplicate to provide a measure of the precision of analysis.

10.5 **Analytical Spikes.** Prepare a matrix spike sample for each sample type as applicable to determine the matrix effect on the recovery efficiency. Concentrations of the spike should be approximately equal to a mid-range calibration standard. The matrix spike sample should be analyzed periodically to measure the precision associated with the analysis. The analyst shall accept percent spike recoveries of 100 ± 25%. Spike recoveries outside of this range should be noted and used with other criteria to evaluate the condition of the analytical run. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run.

11.0 CALIBRATION AND STANDARDIZATION

11.1 Analyze standards prior to each set of samples. The linear regression will be calculated from the plot of all individual calibration points, without including or not forcing through zero, using Target NT Software. A minimum of five calibration standards is required to generate linear regression for target analyte(s). If the calibration curve residuals are greater than 25% deviation from the theoretical value, quadratic curve fitting and/or dropping low/high curve points may be required if data review shows this to be a consistent and more accurate representation of the instrument response. Document in the raw data the technical justification for any deviation and consult with the team leader or designee for direction and for final acceptance or rejection of the data.

11.2 If the curve does not meet requirements perform routine maintenance or prepare a new standard curve (if necessary) and reanalyze

12.0 PROCEDURES

12.1 Set Archon autosampler

12.1.1 Archon System Settings

US Probe Temp	180
Xfer line Temp	180
US Valve Temp	105
Gripper Open	750
Gripper Closed	999
Standby Pol	CLOSED
DesDrn Pol	CLOSED
STOP Pol.	CLOSED
Equilb. Count	0
Equilb. Time	0

12.1.2 Archon System Options

Barcode Scanner	NO
Needle Sparge?	YES
Ign. Vial Type?	YES
Ignore No Vial?	NO
HotWater Rinse?	NO
Vial Checks?	YES
Beep on Error?	YES

12.1.3 Archon Method

Sample Type	Soil
First Vial	1
Last Vial	up to 51
Sample Volume	10
Standard 1 (1uL)	YES
Standard 2	NO
S.PreHeat Stir	NO
Stir	NO
Syring Flushes	0
PreHeat	YES
PreHeat Temp	35
PreHeat Time	1.0
Purge Time	20.0
Desorb Time(m)	0.5
Oper. Mode	Remote
Cycle Timer	0.0
Aux. Timer	0.0
Link to Method	0.0
Soil Purge Flow	40ml/min
Soil Purge Pressure	20psi

12.2 Set Tekmar options

Standby	40°C (30°C by purge)
Purge	20.00min
Dry Purge	2.00min
Desorb Preheat	245°C
Desorb	0.50min at 250°C
Bake	10.00min at 260°C
BGB	OFF
BGB	Delay 0sec
Auto	Drain ON
Valve	180°C
Line	180°C
Mount	100°C
Runs per Sample	1
Purge Flow	40mL/min
Purge Pressure	20psi
Trap	VOCARB 3000
	Containing: Carbopack B
	Carboxen 1000
	Carboxen 1001

12.3 Set GC conditions

12.3.1 Oven:
Initial temp: 40°C
Initial time: 4.00min
Ramp at 15.00°C/min to 280°C
Final time: 10.00min

12.3.2 Front Inlet:
Mode: Split
Initial temp: 180°C
Pressure: 8.50psi (on)
Split ratio: 10.7 : 1
Split flow: 16.1 ml/min
Total flow: 20.6 ml/min

12.4 Set MS conditions

12.4.1 Adjust conditions as needed to optimize system performance and document operating conditions in the instrument run log.
Acquisition mode: Scan (from 10 m/z to 650 m/z)
MS source temp: 230° C
MS quadruple temp: 150°C
Interface temp: 260°C
Multiplier voltage: adjust to give required low standard sensitivity

12.5 Set up the instrument acquisition method. Name the sequence. The sequence includes a sample list documenting the method used and datafiles created. The sequence should be documented n the run files.

12.6 Sample analysis.

12.6.1 Set up autosampler and concentrator methods. Bring samples to room temperature (~22 °C), spike them and place them on autosampler. Generate a mass spectrometer tune report and review. Operating conditions provided above are recommended and may be adjusted to optimize system performance. Analyze all standard, samples, and spiked samples using the same analytical conditions. Document the conditions in the run log.

12.6.2 When data acquisition is complete, data files should be transferred to Target version 4.0 for processing.

13.0 DATA ANALYSIS AND CALCULATION

13.1 Each batch of data should be processed using Target Genie integrator. Integration parameters should be set to minimize the number of manual integrations required yet still result in uniform integration of peaks at all concentration levels. If manual integrations are required, a review code should be assigned to indicate the reason. Review codes are listed below.

Review Code	Explanation
M1	Peak was not automatically integrated by Target, therefore, integrated manually
M2	Peak was automatically integrated; was reintegrated manually to improve sample-to-sample integration consistency.
M3	Incorrect quantification ion peak was integrated; manual integration was done to select the correct peak.
M4	Incorrect monitor ion peak was integrated; manual integration was done to select the correct peak.
M5	Others (specify)

13.2 When data processing is complete, summarize the data using an appropriate form. Formula is provided below for some of the calculations that may be required.

13.2.1 Calculate matrix spike percent recoveries using the following equation:

$$\%\text{Recovery} = \frac{(\text{observed concentration} - \text{background concentration}) \times 100}{\text{expected concentration}}$$

14.0 METHOD PERFORMANCE

14.1 **Coefficient of Determination (r^2).** The coefficient of determination (r^2) for the initial calibration curves should be 0.990 or greater. The curves should be examined closely for

linearity and intercept, particularly for accuracy of quantitation at the low and high ends of the curve. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.2 **Calibration Standards.** The acceptance criterion for the calibration standards is that the accuracy of each standard is 75% to 125% (± 25 % difference) of the nominal value. Calibration standards outside this range are to be noted. Document in the raw data the technical justification for deviations. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.3 **Instrument Surrogate.** Review of the instrument surrogate performance is performed by monitoring instrument surrogate recoveries throughout the run. Inconsistencies in the recoveries may be the result of instrumental changes, or injection error. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run.

14.4 **Sample Surrogate.** Sample surrogate performance is evaluated by averaging the area response throughout the analytical run and calculating %RSD. Inconsistencies in the surrogate peak area may indicate instrumental changes, injection error, or changes in the test-system. Consult with the Team Leader or designee for direction and final acceptance or rejection of the analytical run.

14.5 **Continuing Calibration Verification.** If the accuracy for the amount of quantified analyte is greater than 25% from the nominal value relative to the initial standard curve, the Team Leader should be consulted. Only those samples analyzed before the last acceptable calibration check standard will be used. Consult with the Team Leader or designee for direction and for final acceptance or rejection for the data.

14.6 **Solvent Blanks.** Solvent blanks should show no more than a 5% carryover from a high standard or calibration check standard. If so, two sequential solvent blanks may be necessary to rule out instrumental contamination

14.7 **Matrix Blanks.** Matrix blanks are the basis for determining the LOQ and are monitored at various times in the analytical run. Peaks with greater than 25% of the peak area of the designated LOQ value observed in matrix blanks are indicative of either matrix effect, sample contamination or instrument contamination. Use of solvent blanks prior to the matrix blank may be necessary to rule out instrumental contamination or sample contamination.

14.8 **Control Blanks.** Control blanks are the basis for determining matrix effect (interference or suppression). Peaks with greater than 25% of the peak area of the designated LOQ value observed in control blanks are indicative of either matrix effect, sample contamination or instrument contamination.

14.9 **Limit of Quantitation (LOQ).** The LOQ is equal to the lowest acceptable standard (i.e. % accuracy is ≤ 25 % nominal value) in the calibration curve that is greater than 4 times the level of the matrix blanks.

14.10 **Sample Triplicates.** The analyst shall accept %RSD values < 25%. %RSD values > 25% should be noted. Data used in the final report that is deemed out of control will be

required to have technical justification for why the data is used, documented in the final report and raw data. Consult with the Team Leader or designee for direction, and for final acceptance or rejection of the data.

14.11 Analytical Spikes. The analyst shall accept percent spike recovery values of 100 ± 25%. Spike recoveries outside of this range should be noted. Consult with the Team Leader or designee for direction, and for final acceptance or rejection of the data. Data that are used in final report that is deemed out of control will be required to have a technical justification for why the data are being used, documented in the final report and raw data.

14.12 System Suitability.

14.12.1 Tuning: A mass spectrometer tune report shall be generated before starting each analytical sequence. If the tune parameters do not meet the criteria suggested by the mass spectrometer manual, then the mass spectrometer should be re-tuned. If mass 28 is present in the tune report at >10% relative to mass 69 then an air leak is present in the system. The source of the leak should be isolated and fixed before the sequence is stated; however if a slight air leak is detected, data can be collected, analyzed, and used as long as the data quality objectives are met.

15.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 Dispose of sample vials in low BTU and flammable solvent in high BTU containers. Dispose of glass pipette waste in broken glass containers located in the laboratory.

16.0 RECORDS

16.1 Store chromatograms in the study folder that is labeled with the study number. Include the following information on each chromatogram either in the header or hand written on the chromatogram: injection date, analyst's initial, sample unique number, sample name, preparation date, incubation period, dilution factor (if applicable), and instrument name. Store a copy of the acquisition conditions with the chromatogram packet.

16.2 Plot the calibration curve by non-weighted linear regression and store in the study/project folder.

16.3 Print the sequence and MS tune report from HP Chemstation. The sequence should be initialed and dated, and stored in the run log binder. The MS tune report should be stored in the tune report file. Copy of the sequence and MS tune report should be placed in appropriate study/project folder.

16.4 Summarize data using suitable software and store in the study/project folder.

16.5 Back up electronic data to appropriate medium (primarily CD). Record in the study/project folder the filename and location of backup electronic data.

16.6 List the documents and records generated when performing this method and where they are to be archived.

17.0 ATTACHMENT

17.1 None.

18.0 REFERENCES

18.1 Archon Purge and Trap Autosampler System Operator's Manual, 1996, Varian.
18.2 Tekmar LSC200 Instruction Manual, 1996, Tekmar.
18.3 Agilent MSD Hardware Manual for 5973N, 1999, Agilent.
18.4 Agilent 6890 Series Gas Chromatograph, volumes 1-3, 1999, Agilent

19.0 AFFECTED DOCUMENTS

19.1 None.

20.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

3M ENVIRONMENTAL LABORATORY

Method

Indirect Photolysis Screening Test in Synthetic Humic Water

Method Number: ETS-8-177.0 **Adoption Date:** 10/26/00

Revision Effective Date:

Approved By:

Laboratory Management — Date: OCT 26, 00

Team Leader — Date: Oct 24, 00

Exact Copy of Original

Initial — Date: 3-29-01

1.0 SCOPE AND APPLICATION

1.1 **Purpose.** Chemicals dissolved in natural waters are subject to two types of photoreaction. In the first case, the chemical of interest absorbs sunlight directly and is transformed to products when unstable excited states of the molecule lead to decomposition. In the second case, reaction of dissolved chemical is the result of chemical or electronic excitation transfer from light-absorbing species in the water. Synthetic humic water (SHW) is used for the photolytic reaction matrix because it contains dissolved organic material that absorbs sunlight and produces reactive intermediates that include singlet oxygen ($^1O_2$) that promotes indirect photolysis of the test substance.

1.2 **The method is divided into two phases. Phase one** includes the preparation of SHW. **Phase Two** provides a procedure to calculate solar photolysis rate constants and half-lives of test chemicals in pure water (PW) and SHW. This phase also includes parallel solar irradiation of a radiometer to calculate k_{IO} (the indirect photolysis rate in the test vessel, e.g. 40 mL glass VOA vial) and k_{pE} (the near-surface photolysis rate constant in natural water bodies).

1.3 **Compatible Analytes.** Chemicals that will be subjected to this indirect photolysis screening and testing method include but are not limited to the following compounds:

Compound	Acronym	Compound	Acronym
Perfluorooctanoic acid	PFOA	Perfluorobutanoic acid	PFBA
Perfluorooctanesulfonate	PFOS	Perfluorobutanesulfonate	PFBS
Perfluorooctanesulfonamide	FOSA	Perfluorobutanesulfonamide	FBSA
N-methylperfluorooctanesulfonamide	N-MeFOSA	N-methylperfluorobutanesulfonamide	N-MeFBSA
N-ethylperfluorooctanesulfonamide	N-EtFOSA	N-ethylperfluorobutanesulfonamide	N-EtFBSA
2-(N-methylperfluorooctane sulfonamido) ethyl alcohol	N-MeFOSE-OH	2-(N-methylperfluorobutanesulfonamido) ethyl alcohol	N-MeFBSE-OH
2-(N-ethylperfluorooctane sulfonamido)ethyl alcohol	N-EtFOSE-OH	2-(N-ethylperfluorobutanesulfonamido)ethyl alcohol	N-EtFBSE-OH
1-perfluorooctene	---	1-perfluorobutene	---
Perfluorooctanehydride	1H, C_8-hydride	Perfluorobutanehydride	1H, C_4-hydride
... and other C_4 through C_{10} homologues, and polymeric materials based on the above aforementioned compounds.			

1.4 **Acceptable matrix.** Synthetic humic water (SHW), 0.005 M pH 7.0 Phosphate Buffer.

2.0 SUMMARY OF METHOD

2.1 **Phase One:** A solution of standardized synthetic humic water is prepared by water extraction of commercial humic material. The SHW is buffered at pH 7 with 0.005 M Phosphate buffer to maintain pH and pre-aged in the photoreactor to produce predictable bleaching behavior. It is then diluted at the time of use to a UV-visible absorbance typical of most surface fresh waters (approximately 0.5 AU at 370 nm).

2.2 **Phase Two:** Study samples (5mL aqueous matrix) are prepared in 40 mL glass VOA vials equipped with screw-top caps with septa. Test substance is added to the vials where indicated. (See table below.) Vials are placed in the photoreactor and immersed in a water bath controlled at 25 ± 5 °C. Samples to be exposed are photolyzed in the photoreactor at 261 W/m^2 (300-800 nm) for designated time intervals. A suggested set of time intervals is listed below. Additional timepoints may be added, if necessary, or as assigned by the Team Leader. Time 0 samples will be refrigerated at 1-5 °C. until all timepoints have been completed. Dark controls (unexposed) will also be prepared for each timepoint. Absorbance controls will be used to monitor photo-bleaching of the SHW. Exposed and unexposed absorbance controls will be prepared per timepoint.

2.2.1 Samples to be prepared for each timepoint and for each exposure type:

Description	Test Matrix (Buffer /SHW)	Control Matrix 1 (Buffer/ PW)	Control Matrix 2 (PW)	Test Substance	Post Photolysis Target Analyte Spike	LC/MS Analysis	GC/MS Analysis	UV/Vis Analysis at 370 nm
Sample Rep 1	+	0	0	+	0	A	A	NA
Sample Rep 2	+	0	0	+	0	A	A	NA
Sample Rep 3	+	0	0	+	0	A	A	NA
Sample Spike 1	+	0	0	+	+	A	A	NA
Sample Spike 2	+	0	0	+	+	A	A	NA
Matrix Blank	+	0	0	0	0	A	A	NA
Matrix Blank Spike	+	0	0	0	+	A	A	NA
Control Matrix(#1) blank	0	+	0	0	0	A	A	NA
Control Matrix(#1) sample	0	+	0	+	0	A	A	NA
Control Matrix(#1) spike	0	+	0	+	+	A	A	NA
Control Matrix(#2) blank	0	0	+	0	0	A	A	NA
Control Matrix(#2) sample	0	0	+	+	0	A	A	NA
Control Matrix(#2) spike	0	0	+	+	+	A	A	NA
Absorbance Control	+	0	0	0	0	NA	NA	A
Absorbance Control dup	+	0	0	0	0	NA	NA	A

Where "+" = addition of solution or test substance and "0" = NO addition, A= analysis performed, and NA = no analysis.

Time Point	# of Exposed Samples	# of Unexposed Samples	# of samples for LC/MS Analysis (Exp + Unexp)	# of samples for GC/MS Analysis (Exp + Unexp)	# of samples for UV/Vis Analysis (Exp + Unexp)
0	0	30 (Time 0)	13	13	4
8 hr	30	30	26	26	8
16 hr	30	30	26	26	8
32 hr	30	30	26	26	8
64 hr	30	30	26	26	8
128 hr	30	30	26	26	8
Total # of Samples	150	180	143	143	44

3.0 QUALITY CONTROL-DEFINITION/FREQUENCY/PERFORMANCE CRITERIA

3.1 Blanks

3.1.1 Definitions:

Matrix Blank. A sample of analyte-free matrix (e.g. SHW/buffer) to which all reagents are added in the same volumes or proportions as used in sample processing. For photolysis studies, there are multiple matrix blanks to adequately represent the variables of the study with reference to the matrix (e.g. Exposed, Unexposed and Time 0). The matrix blank is carried through the sample preparation, photolytic and analytical procedures to monitor for contamination during any step. It is also used to establish a chromatographic baseline and monitor for interference or suppression of target analyte(s) from the matrix.

Control Blank. A sample of analyte-free control matrix (such as buffer or ASTM Type II water) to which all reagents are added in the same volumes or proportions as used in sample processing. The control matrix serves as a monitor of the effect of the matrix on the test substance, test analytes and chromatographic behavior. For photolysis studies, there are multiple control blanks to adequately represent the variables of the study with reference to the matrix (e.g. Exposed, Unexposed and Time 0 samples). The control blank is carried through the sample preparation, photolytic and analytical procedures to monitor for contamination during any step. It is also used to establish a chromatographic baseline and monitor for interference or suppression of target analyte(s) from the control matrix.

3.1.2 **Frequency/Performance Criteria:** Listed in the following table:

Matrix ID	Matrix description	Frequency	Performance Criteria
Matrix Blank (Buffer/SHW)	0.01 M Phosphate Buffer, pH 7: Synthetic Humic Water	1 Replicate per light and dark exposure, for each time point and for each analytical methodology.	Any background level of target analyte shall be less than 25% the area counts of the LOQ.
Control Blank #1 (Buffer/PW)	0.01 M Phosphate Buffer, pH 7 : ASTM Type II Water		
Control Blank #2 (PW)	ASTM Type II Water		

3.2 Sample Triplicate

3.2.1 **Definition:** Three aliquots prepared as representatives of the same sample source (e.g. test substance) and carried through all steps of the photolytic study process and analytical procedures in an identical manner. The results from triplicate analyses are used to evaluate variance of the total method, including sample preparation, photolytic process and analysis.

3.2.2 **Frequency/Performance Criteria:** Listed in the following table:

Matrix Description	Frequency	Performance Criteria
Test Matrix *and* test substance	3 Replicates per treatment type	The analyst shall accept %RSDs <25%. Precision values >25% must be documented and justified (if possible).

3.3 Analytical Spike (AS)

3.3.1 **Definition:** A known mass of target analyte(s) in a specified amount of a diluted and/or aliquotted sample. This assumes that an independent estimate of target analyte concentration is available. Analytical spikes are used to evaluate the recovery efficiency of the analyte and the matrix effect.

3.3.2 **Frequency/Performance Criteria:** Listed in the following table:

Matrix Description	Frequency	Performance Criteria
Test Matrix *and* test substance, spiked with target analyte(s) just prior to analysis	2 spiked samples per treatment type (one in lower half of the calibration range, and one in the upper half of the calibration range)	The analyst shall accept accuracy of 100 ± 25%. If accuracy is outside of this range, document and justify, if possible, the reason for the deviation.
Test Matrix *with NO* test substance, spiked with target analyte(s) just prior to analysis	1 Replicate per treatment type (mid-range spike concentration)	
Control Matrix (#1) *and* test substance, spiked with target analyte(s) just prior to analysis		
Control Matrix (#2) *and* test substance, spiked with target analyte(s) just prior to analysis		

3.4 Control Sample

3.4.1 **Definition:** A known matrix containing the test substance carried through the entire sample preparation, photolytic and analytical procedure. This is used to document laboratory performance by comparing recoveries and matrix effects from the different matrices and sample types.

3.4.2 **Frequency/Performance Criteria:** Listed in the following table:

Matrix Description	Frequency	Performance Criteria
Control Matrix (#1) *and* test substance Buffer/PW	1 Replicate per light and dark exposure, for each time point, and for each analytical methodology	The analyst shall accept accuracy of 100 ± 25%. If accuracy is outside of this range, document and justify, if possible, the reason for the deviation.
Control Matrix (#2) *and* test substance PW		

3.5 Absorbance Control

3.5.1 **Definition:** An analyte-free matrix that is carried through the sample processing procedure and analyzed by absorption spectroscopy at 370 nm. It is used to monitor the photo-bleaching rate of the SHW during the testing phase.

3.5.2 **Frequency/Performance Criteria:** Listed in the table below.

Matrix Description	Frequency	Performance Criteria
Control Matrix (#1) Buffer/SHW only	2 Replicates per light and dark exposure, for each time point	Absorbance measured at 370 nm is between 0.01AU-0.05 AU (1 cm pathlength cell)

3.6 Internal Standard/Surrogate

3.6.1 **Internal Standard Definition (applies to LC/MS samples):** A known amount of a compound similar in analytical behavior to the target analyte(s) of interest (e.g. 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8-tridecafluorooctane sulfonic acid (THPFOS) if perfluorooctane sulfonate (PFOS) were to be the target analyte), added to all samples and standards (post-irradiation), and carried through the entire analytical process. It provides a reference for evaluating and controlling the precision and bias of the applied analytical method. Samples are to be quantified using the internal standard.

3.6.2 **Surrogate Definition (applies to LC/MS and GC/MS samples):** A known amount of a compound similar in analytical behavior to the target analyte(s) that may be added to all samples (pre- or post-irradiation, at the discretion of the Team Leader), and carried through the remaining sample preparation and/or analytical process. If added before exposure, it monitors the presence of vial leaks during photolysis, as well as the performance of the purge and trap autosampler and concentrator. Surrogate analysis is used to evaluate the precision and bias of the applied analytical method. Surrogates are not used for quantitation.

3.6.3 **Frequency/Performance Criteria:** Listed in the following table:

Matrix Description	Frequency of Use	Performance Criteria
Sample diluted with 30 mL of **internal standard** compound dissolved in a suitable analytical solvent	Every **LC/MS** sample analyzed	The %RSD for **internal standards** shall be calculated for the area response of all appropriate samples per analytical batch. The analyst shall accept %RSD values of <15%. %RSD values >15% shall be documented and justified, if possible. The % recovery of **internal standards** should be 100 ± 25%. .Surrogates are examined for qualitative information only (i.e., area response should be relatively constant).
Sample with **surrogate** compound spiked into it.	May be added to every **LC/MS** and **GC/MS** sample analyzed	

3.7 Other Definitions.

3.7.1 **Test Substance/Test Analyte:** Any substance (mixture or controlled compound) added or administered to the test system for the purpose of chemical analysis.

3.7.2 **Degradation Product(s):** Secondary analytes of interest produced as a result of chemical reactions during the photolysis and monitored (qualitatively or quantitatively) during the sample analysis procedure.

3.7.3 **Target Analyte(s):** The analyte(s) singled out in the analytical phase of the study is the target analyte. The target analyte may be identical to the test substance used in the experimental phase of the study, a by-product or degradation product that is monitored (qualitatively or quantitatively) during the sample analysis procedure.

3.7.4 **Test Matrix:** The physical matrix in which the study will be conducted.

3.7.5 **Relative Percent Difference (RPD):** A measure of precision defined as the absolute value of the difference of the two values divided by the average of the two values and multiplied by 100.

3.7.6 **Relative Standard Deviation (RSD):** A measure of relative precision for three or more sample replicates; defined as the sample standard deviation divided by the sample average and multiplied by 100. This is expressed as a percent (%RSD).

3.7.7 **Limit of Quantitation (LOQ):** The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The LOQ can be estimated as 10 times the background level in the blank samples. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes, the LOQ analyte concentration is selected as the lowest non-zero standard in the calibration curve that is over four times the background level in the blanks. Sample LOQs are highly matrix-dependent.

4.0 WARNINGS AND CAUTIONS

4.1 Health and Safety Warnings

4.1.1 Wear the proper lab attire for all parts of these procedures. Wear gloves and eye protection at all times.

4.1.2 Handle all solvents in a hood for all parts of the described sample preparation procedure.

4.1.3 For potential hazards of each chemical used, refer to material safety data sheets, packing materials, and 3M Environmental Laboratory's Chemical Hazard Review.

4.1.4 No mouth pipetting is allowed.

4.2 Cautions

4.2.1 The photoreactors are equipped with a continuous flow of cooling water that poses a threat of electrocution when handling the photoreactor during irradiation sequences.

4.2.2 Wear dark protective eyewear when operating the reactor. Do not look directly at the activated lamp. Use caution when handling samples in the reactor; the interior walls of the reactor and exposed glass vials become extremely hot.

5.0 INTERFERENCE

5.1 Contaminants in solvents, reagents, glassware and other sample processing or analysis hardware may cause interference. To reduce the possibility of interference, glassware in which standards are prepared should be pre-rinsed with methanol and allowed to dry before use. The routine analysis of laboratory method blanks must be used to demonstrate that there is no interference under the conditions of the analysis.

6.0 EQUIPMENT

6.1 Analytical balance sensitive to 0.1 mg

6.2 Photoreactor: Suntest CPS+, XLS+, or equivalent, capable of producing 250-765 Watts/m^2, equipped with a xenon arclamp (e.g. 2200 W Xenon Lamp) and the appropriate filters to allow the desired wavelength (e.g. UV Special Suprax® with cut-on at 290 nm, and Quartz dish with IR reflective coating), and a flowing water bath circulating pump or equivalent.

6.3 Water cooler/recirculator capable of maintaining temperature at 25 °C ± 5 °C .

6.4 UV-Visible Spectrophotometer (UV-VIS), equipped with tungsten and deuterium lamps, model 8453, or equivalent

6.4.1 Autosampler: Model G1120A, or 1-cm pathlength cell holder: Model 08451-60104, or equivalent.

6.4.1.1 1-cm pathlength quartz spectrophotometer cell, or equivalent.

6.4.2 Long Path-Length Cell Holder, Hewlett Packard part number 89076C, or equivalent

6.4.2.1 10-cm path length quartz cell equipped with stopcocks, Hewlett Packard Part # 5061-3392, or equivalent.

6.4.3 Data acquisition and analysis software, HP ChemStation for UV-Visible Spectroscopy, G1116AA Rev. B.01.02, or later.

6.5 Data System: A PC capable of controlling the UV-Visible Spectrophotometer system.

6.6 Centrifuge capable of maintaining >2000 rpm for 10 minutes at ambient temperature (22-26 °C).

6.7 Radiometer, capable of detecting and recording irradiation output of the photoreactor for the duration of the study.

6.8 Lab Oven, capable of maintaining 70-80 °C.

7.0 SUPPLIES AND MATERIALS

7.1 40-mL amber and clear glass vials (VOA) with screw caps.

7.2 Crimp cap autovials: 1.5-mL, caps, crimper, and decapper.

7.3 Adhesive-backed labels (return address size) for labeling quartz vials and autovials.

7.4 Disposable glass graduated pipettes, 1 mL to 10 mL.

7.5 Disposable glass Pasteur pipettes and rubber bulbs.
7.6 Glass beakers, various sizes.
7.7 Volumetric flasks, from 10 mL to 1000 mL.
7.8 Hamilton Gastight® syringes (precision ± 1% of the total volume), 5 µL to 1000 µL.
7.9 10-mL Bottle-top dispenser.
7.10 Teflon® filters filter holder apparatus: 0.4 µm pore-size and 0.2 µm pore-size filters (47 mm diameter, Gelman™ or equivalent.
7.11 500-mL glass screw-top containers.

8.0 REAGENTS AND STANDARDS

8.1 **Water/Pure water (PW),** ASTM Type II water at a minimum
8.2 **Methanol (MeOH),** HPLC/SPEC/GC grade from EM Science or equivalent.
8.3 **Acetone,** HPLC/SPEC/GC grade from EM Science or equivalent.
8.4 **Acetonitrile,** HPLC/SPEC/GC grade from EM Science or equivalent.
8.5 **Humic acid, sodium salt,** from Aldrich or equivalent.
8.6 **NaOH,** reagent grade from EM Science™ or equivalent.
8.7 **0.1% NaOH solution Example:** Weigh approximately 1.0 g sodium hydroxide into a weigh boat and transfer quantitatively to a 1 L volumetric flask and dilute to the mark with PW or equivalent.
8.8 **Sulfuric Acid (H_2SO_4),** reagent grade from Fisher or equivalent.
8.9 **Potassium phosphate,** reagent grade from JT Baker or equivalent.
8.9.1 **0.005 M, pH 7.0 Phosphate Buffer. Example:** Weigh 1.36 g KH_2PO_4 into a weigh boat and transfer to a 1 L volumetric flask using PW and dilute to the mark. Transfer the 1 L of solution to a 2 L volumetric flask. Add 600 mL of 0.1% NaOH, adjust the pH to 7.0 ± 0.1 with 0.1% NaOH or dilute H_2SO_4, and dilute to the mark with PW.
8.10 **Method Blank Solutions:**

Method Blank Types	
Matrix ID	**Matrix description**
Test Matrix *Buffer/SHW*	**Example:** 1:10 Solution: Dilute 50 mL Synthetic Humic Water with 0.01 M pH 7.0 Phosphate Buffer solution to 500 mL.
Control Matrix (#1) *Buffer/PW*	**Example:** 1:10 Solution: Dilute 50 mL Pure Water (ASTM Type II) with 0.01 M pH 7.0 Phosphate Buffer solution to 500 mL.
Control Matrix (#2) *PW*	Pure Water (ASTM Type II)

8.11 **Stock Solutions.** Stock solutions for internal standards and spiking solutions are prepared in MeOH at concentrations of approximately 10,000 µg/mL by weighing approximately 0.1 g of the appropriate substance into a 10-mL volumetric flask and bringing to the mark with MeOH. Dilute to make appropriate working solutions.
8.11.1 **Diluting Solution with Internal Standard:** The diluting solution shall contain internal standard at an area response level equivalent to approximately half the

area response of the test substance's high standard in the calibration curve. **Example:** Internal standard solution in MeOH is prepared by diluting 50µL of internal standard stock solution (Section 8.11) to 1 L with MeOH to a nominal concentration of 0.5 AU µg/mL.

8.12 Test Solutions

8.12.1 Test Substance: Prepare a solution of the test substance in acetonitrile. Calculate the concentration so that after the test substance is added to the test vial, no more than 1% of the volume in the test vial will be solvent. (e.g. 50µL added to 5 mL of matrix = 1% v/v) Then measure the absorbance of the test substance solution diluted with buffer/water matrix to the desired concentration. The maximum absorbance at any wavelength greater than 290nm must be < 0.05, when measured in a standard 1-cm pathlength cell. **Example:** A 900 µg/mL solution of test substance in acetonitrile is prepared by weighing 90 mg of test substance into a 100 mL volumetric flask and diluting to the mark with acetonitrile.

9.0 SAMPLE HANDLING

9.1 Record times of initial preparation and dilution on the fluorochemical degradation (photolysis) analysis sample prep sheet (Attachment A).

9.2 Once the test substance solution has been added, the 40 mL VOA sample vials shall be stored and handled cap-side down to minimize loss of any potential volatile analytes. After the exposure period, the LC/MS samples may be turned upright and stored in a cooler at 1-5 °C. After the exposure period, GC/MS samples shall be maintained in an inverted position in a cooler at 1-5 °C until they are loaded onto the autosampler.

9.3 Once the 30-mL aliquot of diluting solvent has been added to the LC/MS photolysis samples, (see Section 12.0), the samples should be analyzed as soon as possible. Alternatively, the samples may be stored at 1-5 °C. Day 0 samples are to be stored at 1-5 °C during the time of sample exposure, and then diluted along with the exposed and unexposed samples just prior to analysis.

10.0 QUALITY CONTROL

10.1 Quality control parameters (and the frequency of use) are included in Section 3.0.

11.0 CALIBRATION AND STANDARDIZATION

11.1 The analytes of interest must be standardized according to laboratory specifications.

11.2 All equipment used, such as the analytical balance, photoreactors, etc. should be calibrated prior to use (daily, weekly, etc.) as specified in its standard operating procedure.

11.3 All samples analyzed will be run against a standard curve containing varying amounts of test substance, and a fixed amount of internal standard or surrogate compound.

12.0 PROCEDURES

12.1 Phase One-Preparation and standardization of synthetic humic water.

12.1.1 Weigh approximately 2.5 g humic acid into a tared 250 mL centrifuge tube.

12.1.2 Add 0.1% NaOH solution to 250 mL.

12.1.3 Screw-cap shut and tape the tube and place horizontally on an orbital shaker. Shake vigorously (e.g. 100-250 rpm) at room temperature for approximately one hour.

12.1.4 Centrifuge the 250 mL of solution at approximately 2000 rpm for 10 minutes or until solution has cleared, and then filter the supernatant through a 0.4µm filter into a clean 500-mL glass screw-top container.

12.1.5 Adjust the pH of the solution to 7.0 with dilute H_2SO_4 or 0.1 % NaOH.

12.1.6 Filter-sterilize the solution through a 0.2µm diameter pore-size filter into a clean 500-mL glass screw-top container.

12.1.7 Seal the container and place cap-side down in the photoreactor chamber.

12.1.8 Expose the SHW 24 hours at 261 W/m^2 to pre-age the solution (equivalent to three day's worth of Miami, Florida sunlight). The EPA's definition of "1 Day" of irradiation is "eight hours." The irradiation intensity of 261 W/m^2 was chosen because it yields the equivalent average optimum natural daylight radiation for 300-400 nm (see the table below):

	Approximate Integrated and Individual Irradiances in W/m^2				
Irradiance Source	250-300 nm	300-400 nm	400-800 nm	340 nm	420 nm
Average Optimum **Natural Daylight**[1]	0.0	27.8	259.0	0.30	0.67
Atlas Photoreactor with integrated irradiance output of 261 W/m^2 300-800 nm using the IR Reflecting and 290 cut-on filters	0.08	27.8	234.36	0.24	0.71

[1]Measured – 25 °N, Miami, Florida (See Reference 18.4)

12.1.9 Aliquot the SHW into a 1-cm quartz UV-VIS cuvette and analyze the absorbance at 370 nm.

12.1.10 Check the pH of the solution using pH paper or a pH probe. Adjust the pH if necessary to 7.0 + 0.1 using a dilute H_2SO_4 solution or 0.1% NaOH solution.

12.1.11 Calculate the dilution factor necessary to decrease the absorbance to approximately 0.5 AU (in a 1-cm pathlength cell) in 1 L of SHW:

$$\frac{0.5}{1\ L} = \frac{A_{\lambda=370}}{x}$$

where: $A_{\lambda=370}$ = the measured absorbance of the SHW at 370 nm
x = the volume of SHW needed to dilute to 1 L with water.

12.1.12 Bring the solution to the exact dilution calculated in 12.1.11 with PW.

12.1.13 Verify that the absorbance is approximately 0.5 AU by aliquoting the diluted SHW into a 1-cm UV-VIS cuvette and taking the absorbance reading at 370 nm.

12.1.14 Transfer the SHW stock solution into an amber, or clear foil-wrapped 1 L glass storage bottle, tightly cap and refrigerate.

12.2 Phase Two

12.2.1 Fill out the "Fluorochemical Degradation (Photolysis) Sample Prep Sheet" (Attachment A) as much as possible, assigning sequential unique ID numbers to each sample to be prepared.

12.2.2 Obtain the appropriate number of clear and amber 40-mL glass vials with caps and cardboard boxes. Label the vial caps using a black permanent marker to distinctly identify samples.

12.2.3 Create labels for each sample to be affixed to the 40-mL vials and the autosampler vials after photolysis is completed. The labels should include the sample number, test substance, matrix, exposure type (e.g. exposed/unexposed/Time 0), date and initials of the analyst.

12.2.4 Aliquot 5.0 mL of Buffer/SHW, Buffer/PW and PW solutions into clear (for exposed samples) and amber (for unexposed and Time 0 samples) 40-mL glass VOA vials. Add test substance to the appropriate vials. See the table below for list of vials, replicates, and sample types. If pre-hydrolysis surrogates are to be used, add them also at this point.

12.2.5 Create one set of samples (listed below) per time point and for each analytical methodology. (LC/MS and GC/MS):

Description	Test Matrix (Buffer/SHW)	Control Matrix 1 (Buffer/PW)	Control Matrix 2 (PW)	Test Substance	Vial Type/Exposure
Sample Rep 1	+	0	0	+	Clear/Exposed
Sample Rep 2	+	0	0	+	Clear/Exposed
Sample Rep 3	+	0	0	+	Clear/Exposed
Sample Spike 1	+	0	0	+	Clear/Exposed
Sample Spike 2	+	0	0	+	Clear/Exposed
Matrix Blank	+	0	0	0	Clear/Exposed
Matrix Blank Spike	+	0	0	0	Clear/Exposed
Control Matrix(#1) blank	0	+	0	0	Clear/Exposed
Control Matrix(#1) sample	0	+	0	+	Clear/Exposed
Control Matrix(#1) spike	0	+	0	+	Clear/Exposed
Control Matrix(#2) blank	0	0	+	0	Clear/Exposed
Control Matrix(#2) sample	0	0	+	+	Clear/Exposed
Control Matrix(#2) spike	0	0	+	+	Clear/Exposed
Sample Rep 1	+	0	0	+	Amber/Unexposed
Sample Rep 2	+	0	0	+	Amber/Unexposed
Sample Rep 3	+	0	0	+	Amber/Unexposed
Sample Spike 1	+	0	0	+	Amber/Unexposed
Sample Spike 2	+	0	0	+	Amber/Unexposed
Test Matrix Blank	+	0	0	0	Amber/Unexposed
Test Matrix Blank Spike	+	0	0	0	Amber/Unexposed
Control Matrix(#1) blank	0	+	0	0	Amber/Unexposed
Control Matrix(#1) sample	0	+	0	+	Amber/Unexposed
Control Matrix(#1) spike	0	+	0	+	Amber/Unexposed
Control Matrix(#2) blank	0	0	+	0	Amber/Unexposed
Control Matrix(32) sample	0	0	+	+	Amber/Unexposed
Control Matrix(32) spike	0	0	+	+	Amber/Unexposed

Where "+" = addition of solution or test substance and "0" = NO addition

Control Matrix(#1)= SHW/Buffer 1:9 v/v
Control Matrix(#2)= PW/Buffer 1:9 v/v

Create one set of samples (listed below) for each time point for UV/VIS analysis:

Description	Test Matrix (Buffer/SHW)	Control Matrix 1 (Buffer/PW)	Control Matrix 2 (PW)	Test Substance	Vial Type/Exposure
Absorbance Control - Light	+	0	0	0	Clear/Exposed
Absorbance Control - Dark	+	0	0	0	Amber/Unexposed

12.2.6 Store the "Time 0" vials in a labeled box at 1-5 °C.

12.2.7 Place all the vials that will go into the photoreactor into an oven set to 70-80 °C. for 5-10 minutes to acclimate the vials, liquid and headspace to photoreactor conditions. Upon removing the vials from the oven, immediately re-tighten the caps and proceed to load the reactor.

12.2.8 Place the amber "unexposed" vials in plastic bags and arrange on the bottom of the photolysis tray (make sure that they don't float once the tray is filled with water). The "unexposed" vials will remain submerged in the cooling water (25 ± 5 °C) during the exposure. (The vials are exposure- and temperature-controlled.)

12.2.9 Place the clear "exposed" vials in the rack in the photoreactor tray cap-side down, and install the rack so that the VOA vial caps will be submerged throughout the duration of exposure.

12.2.10 Prepare the radiometer to read intensity of irradiance over the duration of the exposure. See SOP ETS-9-50.0 for operation of radiometer.

12.2.11 Expose the samples for the designated time intervals at 261 W/m^2. See SOP ETS-9-44.0 for operation of the photoreactor.

12.2.12 Following each exposure interval, remove vials from the photoreactor and store inverted in a cooler at 1-5 °C. After all exposures have been completed, remove all sample vials as well as the "Time 0" vials from the cooler and analyze as a single batch for each instrument.

12.2.13 UV-VIS absorbance control analysis

12.2.13.1 Analyze the pH 7.0 SHW/buffer absorbance controls by UV/Visible absorbance spectroscopy at 370 nm by aliquoting the test solution directly into a 1-cm or greater pathlength quartz cuvette and obtaining the spectra. See SOP ETS-9-46.0 for operation of the UV/VIS instrument. The resultant peak at 370 nm will be analyzed to determine the change in absorbance between the Time 0, exposed and unexposed samples.

12.2.14 LC/MS sample analysis

12.2.15 Dilute the exposed and unexposed samples for all timepoints with 30 mL internal standard solution in methanol (Section 8.11.1). Add spiking solution to the appropriate vials. Invert each vial several times to mix.

12.2.16 Transfer aliquots of LC/MS samples into autovials and then place them in the autosampler for analysis of the parent compound and possible degradation products. Analyze according to ETS-8-181.0.

12.2.17 GC/MS sample analysis

12.2.17.1 Analyze the exposed and unexposed samples for all timepoints as-is by purge and trap GC/MS. Add spiking and surrogate solutions, as required, to the appropriate vials. Analyze according to ETS-8-182.0.

12.2.17.2 *Important:* Maintain vials in the inverted position until they can be placed in the autosampler.

13.0 Data Analysis and Calculations

13.1 Not applicable, as this is a sample preparation and analysis method. Consult the appropriate analytical protocol for guidance regarding data analysis and calculations.

14.0 Method Performance

14.1 Not applicable.

15.0 Pollution Prevention and Waste Management

15.1 Dispose of sample waste by placing in high or low BTU (British Thermal Unit) waste containers as appropriate. Use broken glass containers to dispose of glass pipettes.

16.0 Records

16.1 Print out hard copies of all graphics and data analysis summaries for archiving.

16.2 Sign and date all graphics and label with instrument ID.

16.3 Fill out the sample preparation worksheet(s) documents completely, making sure to include all initials and dates.

16.4 Archive electronic data to compact disc media.

17.0 Attachments

17.1 "Fluorochemical Degradation (Photolysis) Sample Prep Sheet"

18.0 References

18.1 Interpersonal conversation with Carrie O'Connor, Optical Systems Engineer, Atlas Electric Devices.

18.2 "Suntest CPS/CPS+ Spectral Irradiance Distribution," table distributed by Atlas Electric Devices Company, sent via fax by Richard Sherwin, Sales Representative, 26 July, 2000.

18.3 "Atlas Xenon Filter Combination and Sunlight Measurements," information generated by Atlas Electric Devices Company sent via fax by Richard Sherwin, Sales Representative, 26 July, 2000.

18.4 OPPTS 835.5270, Indirect Photolysis Screening Test: Sunlight photolysis in water containing dissolved humic substances.

19.0 AFFECTED DOCUMENTS

19.1 None

20.0 Revisions

Revision Number.	Reason For Revision	Revision Date

Attachment A- Photolysis Sample Prep Sheet

Fluorochemical Degradation (Photolysis) Sample Prep Sheet

TEST ANALYTE: ____________
Lab Request Number: ____________
Nominal Time Interval: ________
Reactor Temperature: ________ °C

Photoreactor ID: ____________
Start Date: ________ Time: ________ Initials ________
Stop Date: ________ Time: ________ Initials ________
Total Reactor Time: _____ days _____ hours _____ min

Cooler Storage ID: ________
Date &Time In ________
Date &Time Out ________
Initials ________

Cooler Storage ID: ________
Date &Time In ________
Date &Time Out ________
Initials ________

		Test Matrix	Control Matrix (1)	Control Matrix (2)	Test Analyte	Spike Solution		Dilution Solvent	Comment
	Date:								
	Time:								
	Initials:								
Sample No.	Light?	Amount (mL)	Amount (mL)	Amount (mL)	Amount (µL)	Solution ID	(µL)	Amount (mL)	
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
	Y								
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	N								
	N								
	N								
	N								
	N								

NOTE: Dark shaded areas require NO additions
NA = not applicable

Test Matrix	Control Matrix (1)	Control Matrix (2)	Test Analyte		Spike Solution		Dilution Solvent	
Solution ID	Solution ID	Solution ID	Solution ID#	Component	Component	Conc. (µg/mL)	Solution ID#	Component
			Conc. (µg/mL)				Conc. (µg/mL)	

Comments: ____

3M ENVIRONMENTAL LABORATORY

EQUIPMENT PROCEDURE

OPERATION AND MAINTENANCE OF THE HEWLETT PACKARD 8453 UV-VISIBLE SPECTROPHOTOMETER

Procedure Number: ETS-9-46.0

Adoption Date: 10/20/00

Exact Copy of Original

3-29-07
Initial Date

Revision Effective Date:

Approved by:

Laboratory Management — Date: 10/20/00

Team Leader — Date: 10/19/00

1.0 SCOPE AND APPLICATION

1.1 This equipment procedure describes the operation, cleaning, and maintenance of the Hewlett-Packard 8453 UV-Visible Spectroscopy System.

2.0 DEFINITIONS

2.1 **Absorbance:** Measure of concentration of material present: expressed as product of molar extinction coefficient (ε), pathlength (b), and concentration (c), written as $A = \varepsilon b c$ (also known as Beer's Law).

2.2 **Cuvette or flow cell:** Transparent receptacle in which sample solutions are introduced into the light path of spectrometers. Usually, two sides are equal (e.g. 1 cm x 1 cm) while the third dimension is elongated, possibly as long as 15 cm. For UV work, the material is quartz. Visible work permits the use of glass or plastic cuvettes.

2.3 **Pathlength:** The distance the light passes through the sample in its holder. In practical terms, the inside dimension of the cuvette (usually 1 cm).

2.4 **Slit width:** Size of opening through which light from cuvette emerges. Choice of slit width depends on wavelength range, separation ability of wavelength selector, and desired isolation of specific wavelength. Slit width is often fixed or automatically programmed.

2.5 **Solvent Cutoff:** The wavelength at which the solvent absorbs a significant portion of the light, causing a loss of signal. In other words, the solvent becomes opaque to the wavelengths being used. This is common in the ultraviolet, rare in the visible.

2.6 **Transmittance:** Ratio of the radiant power transmitted by a sample to the radiant power transmitted by a blank in an equivalent cell or by some other means of compensation for solvent absorption, reflection losses, etc.

2.7 **Visible:** The portion of the electromagnetic spectrum, from 400 to 800 nm, detectable by human eyes.

2.8 **Ultra-violet (UV):** The portion of the invisisble electromagnetic spectrum composed of wavelengths of 10-400 nm. In UV spectrometry we are primarily interested in the near-UV (quartz) region extending from 200 to 380 nm.

2.9 **UV Spectrum:** a plot of wavelength (or frequency) of absorption versus the absorption intensity (absorbance or transmittance).

3.0 DESCRIPTION

3.1 The HP 8453 spectrophotometer is a single-beam, microprocessor-controlled, UV-visible spectrophotometer with collimating optics. The ChemStation® for UV-Visible spectroscopy software running on a PC with Microsoft® NT operating system provides instrument control, data acquisition, and data evaluation.

4.0 IDENTIFICATION

4.1 Hewlett Packard G1103A Serial No. CN93500458

4.2 Hewlett Packard 89090A Serial No. DE14300757

5.0 WARNINGS AND CAUTIONS

5.1 Health and Safety Warnings:

5.1.1 Eye damage may result from directly viewing light produced by deuterium lamps used in detectors and spectrophotometers. Always turn off the deuterium lamp before opening the lamp door on the instrument.

5.1.2 Some adjustments described in the service manual are made with power supplied to the instrument, and protective covers removed. Electricity and heat available at many points may, if contacted, result in personal injury.

5.1.3 Capacitors inside the instrument may still be charged, even though the instrument has been disconnected from its source of supply. Dangerous voltages, capable of causing serious personal injury, are present in this instrument. Use extreme caution when handling, testing, and adjusting.

5.2 Cautions:

5.2.1 Never touch the quartz envelope of the deuterium lamp with your fingers. Fingerprints absorb UV light and may be burnt in, thus reducing lifetime of the lamp.

5.2.2 Quartz sample cells or sample cells with quartz faceplates are required if you want to use the full 190 to 1100 nm wavelength range of the spectrophotometer. Good quality glass cells may be used when working above 350 nm. Disposable plastic sample cells are not recommended for use.

5.2.3 For high precision measurements, wait until the spectrophotometer and the lamps have reached thermal equilibrium. The time required is a function of environmental conditions but the instrument should be ready after 45 minutes. To determine if the spectrophotometer is in stable working condition, the HP 8453 Self- test may be performed. (See section 13.1)

5.2.4 Ensure cell windows are free of fingerprints and other contamination.

5.2.5 Avoid the use of alkaline solutions (pH > 9.5) which can attack quartz and thus impair the optical properties of the flow cells.

5.2.6 Solution in cell should be free of floating particles.

5.2.7 Solution in cell and cell walls should be free of bubbles.

5.2.8 Ensure that solution in cell is homogeneous by thoroughly mixing before measurement.

5.2.9 Blank is measured on the same solvent as sample.

5.2.10 Blank measurement should show a flat baseline.

5.2.11 Cell orientation of blank and sample measurements should be the same.

5.2.12 Ideally, the cell is not removed between sample measurements, which means the cell is filled/rinsed using a pipette or a flow cell is used.

5.2.13 Time between blank and sample measurements should be short.

6.0 SPECIAL INSTRUCTIONS

6.1 None.

7.0 RESPONSIBILITY

7.1 The operator is responsible for routine maintenance and cleaning.

7.2 The person responsible for the equipment (and an alternate) will be identified in the front of the equipment logbook, and are responsible for all routine and non-routine maintenance and associated documentation.

8.0 SUPPLIES AND MATERIALS

8.1 Pozidriv screwdriver
8.2 Isopropanol, reagent grade
8.3 Canister of compressed oil-free air.
8.4 Surgical cotton swabs, lint-free.
8.5 Deuterium lamp assembly, Agilent 8453 (Part No. 2140-0605).
8.6 Lamp, Tungsten G1315A, Agilent 8453A (Part No. G1103-60001).

9.0 INSTRUMENT CLEANING PROCEDURES

9.1 Cleaning the Stray Light Filter. (Recommended at one-yearly intervals or more frequently when operating the spectrophotometer in a particularly dirty environment.)

9.1.1 Turn off the instrument and disconnect the power cord. Take the plastic and sheet metal rear covers off, see "Removing and Replacing Covers" on page 109 of the HP 8453 Service Manual.

9.1.2 Remove any accessory board or MIO board that may be plugged in from the rear side of the instrument.

9.1.3 Remove the upper rear foam block.

9.1.4 Disconnect the shutter cable from the SPM board. Open the screw that fixes the shutter assembly to the optical unit and remove the shutter assembly.

9.1.5 Dampen a lint-free, surgical cotton swab with reagent grade isopropanol and gently swab the surface of the stray light filter. Repeat several times with clean swabs and alcohol each time.

9.1.6 Use a canister of compressed oil-free air to further clean the stray light filter.

9.1.7 Position the shutter assembly above the source lens and fix the screw that holds it at the optical unit, see Figure 39 on page 124 of the Service manual. Connect the shutter cable to the SPM board.

9.1.8 Replace the upper rear and upper front foam blocks.

9.1.9 If available, replace any accessory board or MIO board (plugged in from the rear side of the instrument).

9.1.10 Replace the plastic and sheet metal rear covers. Push the plastic rear cover down so that it locates on both sides, see "Removing and Replacing Covers" on page 109 of the HP 8453 Service Manual.

9.1.11 Reconnect the line power and turn on the instrument. Check that the spectrophotometer passes the self-test, this means that the green light on the front panel comes on and that you can do a blank measurement from the software.

9.2 Cleaning the Source Lens from the Sample Compartment Side. (Recommended at one-yearly intervals or more frequently when operating the spectrophotometer in a particularly dirty environment.)

9.2.1 Turn off the instrument and disconnect the power cord.

9.2.2 Remove any cuvette holder from the sample compartment.

9.2.3 To have better access you may want to take the plastic and sheet metal rear covers off, see "Removing and Replacing Covers" on page 109 of the HP 8453 Service Manual.

9.2.4 Dampen a lint-free, surgical cotton swab with reagent grade isopropanol and gently swab the surface of the source lens. Repeat several times with clean swabs and alcohol each time.

9.2.5 Use a canister of compressed oil-free air to further clean the source lens.

9.2.6 If you have taken the covers off, replace them.

9.2.7 Replace the cuvette holder: Reconnect line power and turn on the instrument. Check that the spectrophotometer passes the self-test, this means that the green light on the front panel comes on and that you can do a blank measurement from the software.

9.3 Cleaning the Spectrograph Lens. (Recommended at one-yearly intervals or more frequently when operating the spectrophotometer in a particularly dirty environment.)

9.3.1 Turn off the instrument and disconnect the power cord.

9.3.2 Remove any cuvette holder from the sample compartment.

9.3.3 To have better access you may want to take the plastic and sheet metal rear covers off, see "Removing and Replacing Covers" on page 109 of the HP 8453 Service Manual.

9.3.4 Dampen a lint-free, surgical cotton swab with reagent grade isopropanol and gently swab the surface of the spectrograph lens. Repeat several times with clean swabs and alcohol each time.

9.3.5 Use a canister of compressed oil-free air to further clean the spectrograph lens.

9.3.6 If you have taken the covers off, replace them. Replace the cell holder in the sample compartment.

9.3.7 Reconnect line power and turn on the instrument. Check that the spectrophotometer passes the self-test, this means that the green light on the front panel comes on and that you can do a blank measurement from the software.

10.0 MAINTENANCE PROCEDURES

10.1 Routine maintenance.

10.1.1 Cleaning the stray light filter. Indicators for a dirty stray light filter include:

10.1.1.1 After exchanging the lamps, the intensity test executed by the ChemStation software still falls below the specified level.

10.1.1.2 One of the stray light tests fails.

10.1.1.3 The photometric accuracy test fails.

10.1.2 Cleaning the lenses that are accessible from the sample compartment side. An indication for dirty lenses is when, after exchanging the lamps, the intensity test executed by the ChemStation software still falls below the specified level.

10.2 Non-routine: Document any non-routine maintenance.

10.2.1 Exchange the deuterium or the tungsten lamp when the intensity test, which is executed through the ChemStation software, falls below the specified level or when one of the lamps no longer ignites. See HP 8453 Service Manual for lamp replacement procedure (p.96).

11.0 OPERATING PROCEDURES

11.1 Powering Up the HP 8453 UV-Visible Spectrophotometer and PC controller.

11.1.1 Switch on the PC and boot the PC operating system.

11.1.2 Switch on the spectrophotometer and wait until the spectrophotometer's indicator light turns green. This process includes the spectrophotometer's self test and takes about one minute.

11.1.3 Launch a measurement session by pressing the operating system's "Start" button and select "Programs", "HP UV-Visible ChemStations", "spectrometer 1 online"

11.1.4 The system is ready to use if the blue "busy" status display on the system's bottom message line turns off. Note: For high precision measurements wait until the spectrophotometer and the lamps have reached thermal equilibrium. The time required is a function of environmental conditions but should be ready after 45 minutes.

11.1.5 The first measurement to perform is a reference measurement. After this alignment you are ready to measure absorbance data and spectra.

11.2 Inserting a Cell.

11.2.1 The HP 8453 is shipped with the standard single-cell holder which accommodates standard cells or flow cells.

11.2.2 Move the locking lever to its up position.

11.2.3 Insert the sample cell, making sure you orient it correctly. The frosted (non-clear) sides of the sample cell *should not* be in the path of the light beam.

11.2.4 Lock the sample cell in place by pushing the locking lever back down.

11.2.5 Small volume flow cells and particularly any cells with less than a 2 mm aperture may require use of the optional adjustable cell holder. This device helps you ensure the cells are properly centered in the light path.

11.3 Entering a Cell's Path Length.

11.3.1 Click "Setup" on the Instrument Panel.

11.3.2 Type the path length in cm in the "Setup Manual" dialog box.

11.3.3 Click "OK" to set the specified path length.

11.4 Starting a Measurement Session.

11.4.1 Start a measurement session by selecting Instrument 1 online from the menu.

11.4.2 Perform a reference measurement. Typically the cell containing the solvent used with your samples is put in the measurement position and a blank measurement performed. To start this measurement, click the "Blank" button on the Instrument Panel or press the spectrophotometer's "Blank" button.

11.4.3 Perform a sample measurement. To get the most precise results, use the same cell in the same orientation to the measurement beam. Flush the cell about three times with the sample solution and start the measurement by clicking the Instrument Panel's "Sample" button or by pressing the spectrophotometer's "Sample" button.

11.5 Setting up a Method for Single Component Analysis.

11.5.1 Choose the "Quantification" task from the data analysis panel.

11.5.2 Enter the used wavelength in the input fields.

11.5.3 If background correction is desired, select "Single Reference Wavelength", "Subtract Average Over a Range" or "Three-point Drop Line" from the background correction combo box.

11.5.3.1 "Single Reference Wavelength" requires the input of one wavelength in the adjacent wavelength edit field on the right side of the combo box.

11.5.3.2 For "Subtract Average Over a Range" or "Three-point Drop Line" you must define the range/baseline by entering the start and end wavelengths in the two adjacent wavelength edit field on the right side of the combo box.

11.5.4 Specify a name for the analyte.

11.5.5 Choose "Concentration" to enter the analyte concentration directly or "Weight & Volume" to have the ChemStation calculate the concentration. Enter the units for the concentration or the weight and volume.

11.5.6 If you want to be prompted for the concentration of the standards during measurement, select "Prompt for Standard Information". In the combo box you can select whether the prompt asks you for the concentration, or calculates the concentration based on volume, weight and purity.

11.5.7 If you have diluted samples and want to correct for dilution, select "Prompt for Dilution Factor" of sample.

11.5.8 Choose the desired calibration curve type.

11.5.9 Select the desired data type and display range of the spectra in the graphical window.

11.5.10 Choose "OK" to close the dialog box.

11.5.11 Perform the following steps if you want to calibrate the method.

11.5.11.1 Measure a blank on the solvent if necessary using the "Blank" button in the instrument panel.

11.5.11.2 Measure the standards using the "Standard" button in the instrument panel. If you have selected one of the prompts, the appropriate values will be requested in a dialog box. The spectrum is displayed automatically in the "Standard Spectra" window as they are measured. Note: There is no fixed limit to the number of calibration standards that can be incorporated into a calibration. However, each of the calibration curve types requires a minimum number of standards of different concentrations, which can be found in Table 7, page 45 of the HP Manual: Understanding Your UV-Visible Spectroscopy System. The ChemStation® software calibrates automatically when at least the minimum number of standards has been measured. A table with the used standards and values as well as calibration curve is displayed.

11.5.11.3 If the calibration is successful, the calibration curve icon of the data analysis panel changes from red to green.

11.6 Measuring and Displaying an Absorbance Spectrum

11.6.1 Select the "Clear" icon using the Toolbar, to delete any spectral data that you do not wish to keep.

11.6.2 Select the "Spectrum/Peaks" task from the Method menu or data analysis panel.

11.6.3 Select the boxes for "Peak/Valley Find" if necessary.

11.6.4 Select "Absorbance" as data type.
11.6.5 Set the display range you want to see in the graphical window.
11.6.6 Choose "OK" to close the "Spectrum/Peaks Parameters" dialog box.
11.6.7 Measure a Blank on the solvent if necessary using the "Blank" button in the instrument panel.
11.6.8 Measure all the samples using the "Sample" button in the instrument panel. The spectra are displayed automatically in the "Sample Spectra" window as they are measured and depending on the selected parameters you will get a table of results.

11.7 Loading Spectra:
11.7.1 Choose "Load" from the "File" menu, then choose the type of spectra that you want to load (Samples or Standards) from the submenu to display the "Load Spectra" dialog box.
11.7.2 If the spectra you wish to load are not in the "File Name" list, select a different directory from the "Directories" list.
11.7.3 Select the spectra you wish to load from the File Name list and choose OK to close the dialog box.

11.8 Saving Spectra:
11.8.1 Choose "Save" from the "File" menu, then choose the type of spectra that you want to save (Samples, Standards or Selected Spectra) from the submenu to display the "Save Spectra As" dialog box.
11.8.2 If you wish to save the spectra in a directory other than the current one, select the new directory from the "Directories" list.
11.8.3 Type the name you wish to save the spectra as in the "File Name" field and choose "OK" to close the dialog box.
11.8.3.1 A valid file name consist of eight alphanumeric characters and the file extension .sd or .std. Usually, the extension .std is used for standards only.
11.8.4 You can also save spectra using the ToolBar.

12.0 RECORDS

12.1 Document all cleaning and maintenance performed on the instrument in the maintenance or run/maintenance logbook. Include a description of the procedure(s) performed, name of person who performed procedure(s), any unusual observations, parts replaced or needing replacement, and whether the procedure was routine or non-routine. Logbooks are archived when complete.

13.0 TESTING, CALIBRATION AND/OR STANDARDIZATION PROCEDURES

13.1 HP 8453 Self-Test:
13.1.1 Make sure that you are in the "Verification and Diagnostics" mode. The mode is indicated on the tool bar of the HP ChemStation® session.
13.1.2 Select the "Self-Test" task in the analysis panel's selection box.
13.1.3 Choose "Self-Test". Start from the "Task" menu or click "Start" to start the self-test.
13.1.4 The self-test results will be displayed in a window with pass/fail criteria.

13.2 Calibrating for a single component analysis.

13.2.1 Calibration for single component analysis is based on the measurement of standard samples with known concentrations. During the calibration process, the software calculates the calibration coefficients, which are then used for the quantification of unknown samples.

13.2.2 The status for calibration can be seen in the data analysis panel:

13.2.2.1 Uncalibrated: RED dashed calibration curve icon.

13.2.2.2 Calibrated: GREEN continuous calibration curve icon.

13.2.3 To calibrate for single component analysis:

13.2.3.1 Load or set up a method for the "Quantification" task.

13.2.3.2 If the "Standard" spectra window is not displayed, choose "Show" standards in the data analysis panel.

13.2.3.3 You can either load the standards from file or measure them.

13.2.3.4 To measure standards:

13.2.3.4.1 Measure a bank on the solvent if necessary using the "Blank" button in the instrument panel.

13.2.3.4.2 Measure the standards using the "Standard" button in the instrument panel. If you have selected one of the prompts in the method, the appropriate values will be requested in a dialog box.

13.2.4 The spectra are displayed automatically in the "Standard Spectra" window as the standards are measured. A minimum number of standards is required, depending on the selected calibration curve. The ChemStation® software calibrates automatically when at least the minimum number of standards have been measured. A table with the used standards and values as well as a calibration curve is displayed.

13.2.5 If the calibration is successful, the calibration curve icon of the data analysis panel changes from red to green.

14.0 REFERENCES

14.1 Definitions obtained from www.spectroscopymag.com.

14.2 HP Manual: Understanding Your UV-Visible Spectroscopy System, Hewlett-Packard: Wilmington, DE, 1997. Part No. G1115-90005.

14.3 HP 8453 UV-Visible Spectrophotometer Operator's Manual, Hewlett-Packard: Wilmington, DE, 2000. Part No. G1115-90012.

14.4 HP 8453 UV-Visible Spectrophotometer Service Manual, Hewlett-Packard: Wilmington, DE, 1998. Part No. G1115-90003.

15.0 AFFECTED DOCUMENTS

15.1 None.

16.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

3M ENVIRONMENTAL LABORATORY

EQUIPMENT PROCEDURE
ROUTINE MAINTENANCE OF ARCHON PURGE AND TRAP AUTOSAMPLER, TEKMAR PURGE AND TRAP CONCENTRATOR AND AGILENT GAS CHROMATOGRAPH/MASS SPECTROMETER

Procedure Number: ETS-9-49.D

Adoption Date: 10/20/00

Exact Copy of Original
3-29-07
Initial Date

Revision Date:

Approved by:

Laboratory Manager — Date: 10/20/00

Team Leader — Date: Oct 20, 00

1.0 SCOPE AND APPLICATION (USE NUMBERED TIER I)

1.1 This equipment procedure describes the maintenance required for optimal operation of the Archon Purge and Trap Autosampler, Tekmar Purge and Trap Concentrator and Agilent gas chromatograph / mass spectrometer (GC/MS) system. Specific items requiring routine maintenance include occasional tightening vial escalator's nuts and refilling the Standard Vial and water bottle in the Archon autosampler and periodic cleaning of the mass spectrometer ion source.

2.0 DEFINITIONS

2.1 None.

3.0 DESCRIPTION

3.1 Archon purge and trap autosampler equipped with Tekmar purge and trap concentrator and Agilent gas chromatograph and mass spectrometer.

4.0 IDENTIFICATION

4.1 System : "Rufus". (An equivalent system may be used).

- 4.1.1 Autosampler: serial number 13006, Varian, Archon
- 4.1.2 Concentrator: serial number 90297002, LSC2000, Tekmar
- 4.1.3 GC: serial number US00034972, 6890 G1530A, Agilent
- 4.1.4 MS: serial number US01180105, 5973N G2589A, Agilent
- 4.1.5 PC: serial number US94850812, D6720T, HP Kayak XA

5.0 WARNINGS AND CAUTIONS

5.1 Health and Safety Warnings:

- 5.1.1 Cooling the Tekmar before removing the side cover for maintenance prevents contact burns.
- 5.1.2 Turning off power source for Tekmar before removing the side cover will prevent electric shock.

5.2 Cautions:

- 5.2.1 It is recommended that a grounded antistatic wrist strap be worn while disconnecting all wires, contacts, or cables which are connected to printed circuit boards within Archon autosampler, Tekmar concentrator or MS analyzer.
- 5.2.2 To prevent the breakage of the Standard Vial on Archon autosampler, during the refill, do not use any tool and do not overtighten the thumbnut.
- 5.2.3 Never add oil while the foreline pump is on.

6.0 SPECIAL INSTRUCTIONS

6.1 Not applicable.

7.0 RESPONSIBILITY

7.1 Routine maintenance procedures may be performed by a primary custodian, and by any analyst who has been trained to perform these maintenance procedures by a primary custodian.

8.0 SUPPLIES AND MATERIALS

8.1 Graphite Ferrules, 0.4 mm I.D. for 0.25 mm columns
8.2 Abrasive paper, Hewlett-Packard, part no. 5061-5896
8.3 Alumina abrasive powder, Hewlett-Packard, part no. 8660-0791
8.4 Acetone, reagent grade
8.5 Dichloromethane, reagent grade
8.6 Methanol, purge and trap grade
8.7 Gloves (clean, lint-free, cotton), Hewlett-Packard, part no. 8650-0030 (large); 8650-0029 (small)
8.8 Cotton swabs
8.9 Chem-wipes
8.10 Glass beakers
8.11 Sonicator
8.12 Base deactivated 2 mm ID gooseneck splitless injection port liners, Restek Corporation, part #20796-210.5, or equivalent
8.13 11 mm diameter Thermogreen LB2 septa, Supelco, part #23163, or equivalent
8.14 Viton injection port o-rings, Restek Corporation, part #20377, or equivalent
8.15 Septum wrench, Hewlett-Packard, part #19251-00100
8.16 Tweezers

9.0 CLEANING PROCEDURES

N/A

10.0 MAINTENANCE PROCEDURES

10.1 Routine: Tighten the elevator's assembly nuts when Archon autosampler displays error message " Elevator not homed position ".
- **10.1.1** Stop autosampler run by pressing STOP button on the front display twice.
- **10.1.2** Open the back cover of autosampler
- **10.1.3** Tighten top and bottom nuts on the elevator's assembly, do not over tighten them.
- **10.1.4** Close the back cover of autosampler

10.2 Routine: Fill the water bottle, empty the waste bottle.
10.3 Routine: If internal standards or surrogates are to be used, be certain the Standard Vial is filled with the required internal standard or surrogate.
- **10.3.1** Turn the helium gas "OFF" with the toggle switch.
- **10.3.2** Push "System" key, choose Maintenance, Standard Control, Front Park.
- **10.3.3** Grasp the vial and loosen the black thumbnut. Slide the vial down.

10.3.4 Clean the vial with methanol, dry it thoroughly and fill the vial with approximately 5 ml of standard or surrogate

10.3.5 Slide the vial back up into standard mount. Finger-tighten thumbnut until it is snug. Do not use any tool and do not overthighten.

10.3.6 Turn the helium gas into ON position. Prime Standard Loop.

10.4 Routine: GC/MS foreline pump maintenance.

10.4.1 Examine the oil level window daily. If the oil level is near or below the lower line then add foreline pump oil. Never add oil while the foreline pump is on.

10.4.1.1 Vent the MSD according to the MSD Hardware Manual.

10.4.1.2 Remove the fill cap.

10.4.1.3 Add pump fluid until the oil level in the window is near, but not above, the upper line.

10.4.1.4 Reinstall the fill cap.

10.4.1.5 Pump down the MSD according to the MSD Hardware Manual

10.4.2 Change foreline pump oil every 6-12 months according to the MSD Hardware manual.

10.5 Nonroutine: Document any nonroutine maintenance in the instrument's maintenance logbook.

11.0 OPERATING PROCEDURES

11.1 For operating procedures, refer to an appropriate analytical method, or to the Archon Purge and Trap Autosampler System Operator's Manual, Tekmar LSC200 Instruction Manual and the Hewlett-Packard MSD Hardware Manual for HP 5973N & HP 6890 Series Mass Selective Detectors.

12.0 RECORDS

12.1 Document any maintenance performed on the instrument in the maintenance or run/maintenance logbook. Include a description of the procedure(s) performed, any unusual observations, parts replaced or needing replacement, and whether the procedure was routine or non-routine. Be sure to date and initial the entry. Logbooks are archived when complete.

13.0 TESTING, CALIBRATION AND/OR STANDARDIZATION PROCEDURES

13.1 After cleaning the source and allowing sufficient time for the vacuum to pump down and the mass spectrometer to equilibrate to operation temperature, run an autotune; check for improved performance and for the presence or absence of air leaks. A tune report can also be used to check for leaks after performing injection port maintenance.

14.0 REFERENCES

14.1 Archon Purge and Trap Autosampler System Operator's Manual

14.2 Tekmar LSC200 Instruction Manual

14.3 Hewlett-Packard MSD Hardware Manual for HP 5973N & HP 6890 Series Mass Selective Detectors.

15.0 AFFECTED DOCUMENTS

15.1 None.

16.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

Appendix B: Chemical Characterization

This appendix includes chemical characterization information for both reference substances and control substances.

Chemical Characterization (Reference Substances)

Substance	N-EtFOSE alcohol	PFOS K Salt	FOSA
IUPAC Name	2-(*N*-ethylperfluoro-octanesulfonamido)ethyl alcohol	Potassium perfluorooctanesulfonate	Perfluoroctane-sulfonamide
Chemical Formula	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	$C_8F_{17}SO_3K$	$C_8F_{17}SO_2NH_2$
Identifier	1691-99-2*	2795-39-3*	754-91-6*
Source	3M Specialty Chemicals	3M Specialty Chemicals	3M Specialty Chemicals
Expiration Date	2002	2001	2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	SE035	SD009	SE027
Physical Description	White wax	White powder	White wax
Purity	97.8%	86.4	95%≤
Substance	**N-EtFOSA**	**PFOA**	**C_8 Terminal Hydride**
IUPAC Name	*N*-ethylperfluoro-octanesulfonamide	Perfluorooctonic acid, Ammonium Salt	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8, 8 heptadecafluorooctane
Chemical Formula	$C_8F_{17}SO_2NHCH_2CH_3$	$C_7F_{15}CO_2NH_4$	$C_8F_{17}H$
Identifier	4151-50-2*	2395-00-8 *	335-65-9*
Source	3M Specialty Chemicals	3M Specialty Chemicals	Aldrich Chemical
Expiration Date	2002	2002	2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	SD012	1	04307PN, TNA-2983
Physical Description	White wax	White powder	Clear ambient liquid
Purity	95%≤	97%≤	99%
Substance	**C_7 Perfluoroheptenes (90/10 mix)**	**C_7 Hydride**	**C_6 Hydride**
IUPAC Name	10% 2-Perfluoroheptene, 90% Perfluoroheptene	1,1,2,2,3,3,4,4,5,5,6,6,7,7,7 pentadecafluoroheptane	1,1,2,2,3,3,4,4,5,5,6,6,6 tridecafluorohexane
Chemical Formula	$C_4F_9CF{=}C_2F_5$, $C_5F_{11}CF{=}CF_2$	$C_7F_{15}H$	$C_6F_{13}H$
Identifier	355-63-5*	27213-61-2*	355-37-3*
Source	Lancaster Synthesis	Lancaster Synthesis	Lancaster Synthesis
Expiration Date	2005	2005	2005
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	90004250, TNA 3025	9005911, TNA-3026	90005941, TNA-3027
Physical Description	Clear ambient liquid	Clear ambient liquid	Clear ambient liquid
Purity	100%	97%	98%

Reference Substances (continued)

Reference Substance	C_8 Hydride/Olefin Mix	PFBS	C_4 Terminal Hydride
IUPAC Name	1,1,1,2,2,3,3,4,4,5,5,6,6,7,8,8,8 pentadecafluorooctane, 2-perfluorooctene	Perfluorobutanesulfonate, potassium salt	1,1,2,2,3,3,4,4,4 nonafluorobutane
Chemical Formula	$C_6F_{13}CFHCF_3$, $C_6F_{13}CF=CF_2$	$C_4F_9SO_3K$	C_4F_9H
Identifier	TCR-99030-18	29420-49-3*	375-17-7*
Source	3M Specialty Chemicals	3M Specialty Chemicals	Crescent Chemical
Expiration Date	6/6/99	2002	2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	1	TCR-99030-028	6A-46, TNA-3997
Physical Description	Clear ambient liquid	White Powder	Clear ambient liquid
Purity	85% C_8 Hydride, 15% C_8 Olefin	97%≤	99%
Reference Substance	**C_4 Interior Olefin**	**C_3 Terminal Hydride**	**C_2 Terminal Hydride**
IUPAC Name	2-Perfluorobutene	1,1,2,2,3,3,3 heptafluoropropane	1,1,2,2,2 pentafluoroethane
Chemical Formula	C_4F_8	C_3F_7H	C_2F_5H
Identifier	360-89-4*	2252-84-4*	354-33-6*
Source	Lancaster Synthesis	Lancaster Synthesis	Lancaster Synthesis
Expiration Date	2002	2010	2010
Storage Conditions	Frozen	Flammable	Flammable
Chemical Lot Number	G00195, TNA-4298	G0062B, TNA-4294	G00492, TNA-3021
Physical Description	Clear ambient liquid	Gas	Gas
Purity	97%	97%	99%

*CAS Number

Chemical Characterization (Control Substances)

Control Substances	PFCH	THPFOS	Pentafluorobenzene
Structure	C_6F_{12}	$C_8F_{13}H_4SO_3K$	C_6HF_5
IUPAC Name	Perfluorocyclohexane	Potassium 3,3,4,4,5,5,6,6,7,7,8,8,8 tridecafluorosulfonate	Pentafluorobenzene
Use	Surrogate Standard For GC/MS analysis	Internal Standard for LC/MS analysis	Instrumental Surrogate Standard For GC/MS analysis
Source	Aldrich Chemical	SynQuest Labs	Restek Corp.
Expiration Date	2005	2003	6/2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	01911AU	99022-31, TNA-4154	A013256
Physical Description	Colorless Moist Solid	White powder	Methanol solution
Purity	97%	95% <	99% (2500 µg/mL ± 0.2%)

Control Substances	Chlorobenzene-d_5	Toluene-d_8	Dibromofluoromethane
Structure	C_6ClD_5	C_7D_8	$CHBr_2F$
IUPAC Name	Chlorobenzene-d_5	Toluene-d_8	Dibromofluoromethane
Use	Instrumental Surrogate Standard For GC/MS analysis	Instrumental Surrogate Standard For GC/MS analysis	Instrumental Surrogate Standard For GC/MS analysis
Source	Restek Corp.	Restek Corp.	Restek Corp.
Expiration Date	6/2002	2/2002	2/2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	A013256	A012973	A012973
Physical Description	Methanol solution	Methanol solution	Methanol solution
Purity	99% (2500 µg/mL ± 0.2%)	99% (2500 µg/mL ± 0.2%)	99% (2500 µg/mL ± 0.2%)

Control Substances	1,4 Difluorobenzene	4-Bromofluoro-benzene	1,4-Dichlorobenzene-d_4
Structure	$C_6H_4F_2$	C_6H_4BrF	$C_6Cl_2D_4$
IUPAC Name	1,4 Difluorobenzene	4-Bromofluoro-benzene	1,4-Dichlorobenzene-d_4
Use	Instrumental Surrogate Standard For GC/MS analysis	Instrumental Surrogate Standard For GC/MS analysis	Instrumental Surrogate Standard For GC/MS analysis
Source	Restek Corp.	Restek Corp.	Restek Corp.
Expiration Date	6/2002	2/2002	6/2002
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	A013256	A012973	A013256
Physical Description	Methanol solution	Methanol solution	Methanol solution
Purity	99% (2500 µg/mL ± 0.2%)	99% (2500 µg/mL ± 0.2%)	99% (2500 µg/mL ± 0.2%)

Appendix C: Kinetics Model and Kinetic Calculations

This appendix presents the mathematical description of the kinetics model employed in this study and the application of this model in the determination of the estimated half-lives presented.

Kinetics Model

C1. Reaction Components and Rates

The arguments below are based on the following idealized set of reactions representing the photodegradation of a parent compound P and its products A_m, which number N. The actual reactions that occur are subsumed in these equations, and are assumed to proceed with pseudo-first order rates k_{Pm} (for the parent) and k_{Am} (for the products).

$$P + photon \xrightarrow{k_{Pm}} n_m A_m + Y_{m1} \qquad (m = 1 \text{ to } N) \tag{C1}$$

$$A_m + photon \xrightarrow{k_{Am}} Y_{m2} \qquad (m = 1 \text{ to } N) \tag{C2}$$

where "photon may either represent a photon of light or it may represent some other species in solution that reacted with a photon to produce a new reactive species and the general symbols Y_{m1} and Y_{m2} represent all the other photolysis products.

C2. Parent Compound Concentrations

Equation C1 indicates that the pseudo-first order differential change in the parent concentration P at a constant flux of light or a constant concentration of radicals is given by

$$dP = -P\left(\sum_{m=1}^{N} n_m\, k_{Pm}\right)dt \tag{C3}$$

which is equivalent to the separable differential equation

$$\frac{dP}{P} = -\left(\sum_{m=1}^{N} n_m\, k_{Pm}\right)dt \tag{C4}$$

Equation C4 may be directly integrated to obtain the general solution

$$\ln[P] = \left(-\sum_{m=1}^{N} n_m\, k_{Pm}\, t\right) + C \tag{C5}$$

With the initial condition $P(t=0) \equiv P_0$, the specific solution to Equation C4 is

$$P = P_0 \exp\left(-\sum_{m=1}^{N} n_m\, k_{Pm}\, t\right) \equiv P_0\, e^{-k_P t} \tag{C6}$$

using the additional definition of the total parent photolysis rate

$$k_P \equiv \sum_{m=1}^{N} n_m \, k_{Pm} \quad . \tag{C7}$$

Equation C6 can be re-written in a form that allows a least-squares estimate of the total parent hydrolysis rate:

$$k_P t = -\ln\left(\frac{P}{P_0}\right) \tag{C8}$$

Using the initial $(t = 0)$ measured value of the parent concentration P_0 and later values P measured at later times t, one can calculate and plot the (linear) quantity $[-\ln (P/P_0)]$ versus time and obtain a least -squares estimate of the slope of the line. The resulting slope is the least-squares estimate $\hat{k}_P$ of the total parent photolysis rate.

Equation C6 indicates that over a period of time $T^{1/2}_p$ (the parent half-life) the parent concentration P is reduced through hydrolysis by a factor of two, where

$$T^{1/2}_p = \frac{\ln(2)}{k_P} \tag{C9}$$

A least squares estimate $\hat{T}^{1/2}_p$ of the parent photolysis half-life is therefore available from

$$\hat{T}^{1/2}_p = \frac{\ln(2)}{\hat{k}_P} \quad . \tag{C10}$$

C3. Product Compound Concentrations

The pseudo-first order differential changes in the product concentrations A_m (using Equations C2 and C6) are

$$dA_m = \left(n_m k_{Pm} P - k_{Am} A_m\right) dt = \left(n_m k_{Pm} P_0 \, e^{-k_P t} - k_{Am} A_m\right) dt \tag{C11}$$

and the (first order, non-separable) differential equation governing the product concentrations is

$$\frac{dA_m}{dt} + k_{Am} A_m = n_m k_{Pm} P_0 \, e^{-k_P t} \quad . \tag{C12}$$

The "standard form" of Equation C12 is

$$A_m' + S(t)\,A_m = Q(t) \tag{C13}$$

where the "function" $S(t)$ is actually a constant:

$$S(t) = k_{Am} \tag{C14}$$

and

$$Q(t) = n_m k_{Pm} P_0\, e^{-k_P t} \quad . \tag{C15}$$

The general solution A_m to Equation C12 is contained in

$$A_m\, e^{\int S(t)\,dt} = \int Q(t)\, e^{\int S(t')\,dt'}\, dt + C \tag{C16}$$

where

$$e^{\int S(t)dt} = e^{\int S(t')dt'} = e^{k_{Am}\int dt} = e^{k_{Am}t} \tag{C17}$$

and

$$\int Q(t)\, e^{\int S(t')dt'}\, dt \;+\; C \;=\; n_m k_{Pm} P_0 \int e^{k_{Am}t}\, e^{-k_P t} dt \;+\; C \tag{C18}$$

There are two cases of Equation C18 to consider. In the circumstance that $k_{Am} = k_P$, which occurs only when the rate of the m^{th} product is identical to the total parent photolysis rate, the general solution to Equation B18 is

$$\text{(for } k_{Am} = k_P\text{)}$$

$$A_m\, e^{k_P t} = n_m k_{Pm} P_0\, t + C \tag{C19}$$

and, using the initial condition $A_m(t=0) = A_{m0}$, the specific solution to Equation18 is

$$\text{(for } k_{Am} = k_P\text{)}$$

$$A_m = \left(n_m k_{Pm} P_0\, t + A_{m0}\right) e^{-k_P t} \quad . \tag{C20}$$

We note that when $k_{Am} = k_P = 0$ (that is, when both the parent and potential product are photolytically stable), Equation C7 requires (also) that $k_{Pm} = 0$, so Equation C20 becomes

$$A_m = A_{m0} \qquad \text{(C21)}$$

indicating, as required, that the product concentration does not change with time.

The circumstance $k_{Am} = k_P$ is highly improbable, and is neglected in the remainder of this discussion. However, the reader should bear in mind that the expressions derived below do not hold when the parent photolysis rate k_P and the product photolysis rate k_{Am} approach each other.

In the more probable case, for which $k_{Am} \neq k_P$ (i.e. that the rate of the m^{th} product is different from the total parent rate), the general solution to Equation C18 is

$$A_m\, e^{k_{Am}t} = \frac{n_m k_{Pm} P_0}{k_{Am} - k_P} e^{(k_{Am} - k_P)t} + C \qquad \text{(C22)}$$

and the specific solution to Equation C18 with the initial condition $A_m(t=0) = A_{m0}$ is

$$A_m = \left(A_{m0} + \frac{n_m k_{Pm} P_0}{k_P - k_{Am}} \right) e^{-k_{Am}t} - \frac{n_m k_{Pm} P_0}{k_P - k_{Am}} e^{-k_P t} \quad . \qquad \text{(C23)}$$

Of greatest interest here is the case in which the product compounds are known to be photolytically stable, that is, when $k_{Am} = 0$ for all m. In this case, Equation C23 becomes

(for stable products)

$$A_m = A_{m0} + \frac{n_m k_{Pm} P_0}{k_P} \left(1 - e^{-k_P t} \right) . \qquad \text{(C24)}$$

C4. Relationships Between the Parent and Compound Concentrations

Equations C7 and C24 can be combined to obtain

(for stable products)

$$k_P = \sum_{m=1}^{N} n_m\, k_{Pm} = \frac{k_P}{\left(1 - e^{-k_P t}\right)} \sum_{m=1}^{N} \frac{(A_m - A_{m0})}{P_0} \qquad \text{(C25)}$$

so that

(for stable products)

$$\left(1-e^{-k_P t}\right)=\sum_{m=1}^{N}\frac{\left(A_m-A_{m0}\right)}{P_0} \qquad \text{(C26)}$$

or

(for stable products)

$$k_P t=-\ln\left[1-\sum_{m=1}^{N}\frac{\left(A_m-A_{m0}\right)}{P_0}\right] \qquad \text{(C27)}$$

If the changes in the product concentrations are all small compared to the original parent concentration, that is, if

$$\left|\sum_{m-1}^{N}\frac{A_m-A_{m0}}{P_0}\right|<<1, \qquad \text{(C28)}$$

we may use the expression (valid for $-1 \le X \le 1$)

$$\ln(1+X)=X-\frac{1}{2}X^2+\frac{1}{3}X^3-\frac{1}{4}X^4+..... \qquad \text{(C29)}$$

and Equation C23 becomes

(for stable products and $\left|\sum_m A_m-A_{m0}\right|<<P_0$)

$$k_p t\cong-\left(-\sum_{m=1}^{N}\frac{A_m-A_{m0}}{P_0}\right) \qquad \text{(C30)}$$

or

(for stable products and $\left|\sum_m A_m-A_{m0}\right|<<P_0$)

$$k_p t\cong\sum_{m=1}^{N}\frac{A_m-A_{m0}}{P_0}\ . \qquad \text{(C31)}$$

C5. Parent Half-Life Estimates Based on Limits of Quantification of the Products

In every experimental determination of k_P, there is some set of values A_m^{LOQ} (the "limits of quantitation") below which the product concentrations A_m cannot be reliably measured. If during an experiment carried out over the period of time Δt all the product concentrations A_m remain below their limits of quantitation, then the maximum possible value of the rate k_P is obtained by assuming (for all the products) that 1) $A_{m0} = 0$ and 2) at time $t = \Delta t$, the product concentrations have increased to the values $A_m = A_m^{LOQ}$. With these assumptions, the experimental data indicate that the reaction rate k_P is less than some maximum value $(k_P)_{max}$ as follows:

(for photolytically stable products at concentrations below the limits of quantitation)

$$k_P \le (k_P)_{max} = \frac{1}{P_0 \, \Delta t} \sum_{m=1}^{N} A_m^{LOQ} . \qquad \text{(C32)}$$

Under the same circumstances and assumptions, the experimental data indicate that the parent half-life $T_p^{1/2}$ (see Equation C9) is greater than the value $(T_p^{1/2})_{min}$ as follows:

(for photolytically stable products at concentrations below the limits of quantitation)

$$T_p^{1/2} \ge (T_p^{1/2})_{min} = \frac{\ln(2)}{(k_P)_{max}} = \Delta t \; P_0 \ln(2) \left[\sum_{m=1}^{N} A_m^{LOQ} \right]^{-1} \qquad \text{(C33)}$$

The reader should note that Equations C32 and C33 are valid only when both 1) the products are stable and 2) the concentrations of *all* the potential products are measured. Otherwise, the quantity $(k_P)_{max}$ in Equation C32 may not actually represent the maximum possible value of the rate constant k_P, and the related result in Equation C33 for $(T_p^{1/2})_{min}$ is also questionable.

C6. Parent Half-Life Estimates Based on Limits of Quantification and Experimental Precision of Product Concentrations

In certain experiments, some products are present at quantifiable but essentially constant concentrations over the time (Δt) of the experiment. In this case, it is the experimental precision of the measured product concentrations, rather than the limits of quantitation, which contribute to the estimate of the maximum value of the parent hydrolysis rate k_P. If the set of concentrations measured for the m^{th} product have the mean value μ_m and

standard deviation σ_m, the data do not exclude the possibility that the product concentration increased from the initial value $\sigma_m - \mu_m$ to the value $\sigma_m + \mu_m$ at time t = Δt. Taking this possibility to be the actual case for the measured products, the maximum value of the quantity $(A_m - A_{m0})$ is $2\sigma_m$. This reasoning suggests that the following estimate of the maximum parent photolysis rate is appropriate:

(for stable products at either 1) constant measured concentrations with standard deviation σ_m or 2) concentrations below the limits of quantitation)

$$k_P \leq (k_P)_{max} = \frac{1}{P_0 \Delta t}\left[\sum_{\text{Below LOQ}} A_m^{LOQ} + \sum_{\text{Constant}} 2\sigma_m\right]. \qquad \text{(C34)}$$

Under these circumstances and assumptions, the experimental data indicate that the parent half-life $T_p^{1/2}$ is greater than the value $(T_p^{1/2})_{min}$ as follows:

(for stable products at either 1) constant measured concentrations with standard deviation σ_m or 2) concentrations below the limits of quantitation)

$$T_p^{1/2} \geq (T_p^{1/2})_{min} = \frac{\ln(2)}{(k_P)_{max}} = \Delta t \; P_0 \ln(2)\left[\sum_{\text{Below LOQ}} A_m^{LOQ} + \sum_{\text{Constant}} 2\sigma_m\right]^{-1}. \qquad \text{(C35)}$$

The reader should note that Equations C34 and C35 are valid only when both 1) the products are photolytically stable and 2) the concentrations of *all* the potential products are measured.

C7. Parent Half-Life Estimates Based on the Experimental Precision of Parent Concentrations

In certain experiments, the concentration of the parent remains essentially constant over the time (Δt) of the experiment. In this case, it is the experimental precision of the measured parent concentrations that determines the maximum value of the parent hydrolysis rate k_P. If the set of concentrations measured for the parent have the mean value μ_P and standard deviation σ_P, the data do not exclude the possibility that the product concentration increased from the initial value $\mu_P - \sigma_P$ to the value $\mu_P + \sigma_P$ at time t = Δt. This reasoning suggests that the following estimate of the maximum parent photolysis rate is appropriate:

(for essentially constant parent concentrations with mean value μ_P and standard deviation σ_P)

(C36)

$$k_P \le (k_P)_{max} = \frac{2\sigma_P}{\mu_P \, \Delta t}.$$

Under these circumstances and assumptions, the experimental data indicate that the parent half-life $T^{1/2}_p$ is greater than the value $(T^{1/2}_p)_{min}$ as follows:

(for essentially constant parent concentrations with mean value μ_P and standard deviation σ_P)

$$T^{1/2}_p \ge (T^{1/2}_p)_{min} = \frac{\ln(2)}{(k_P)_{max}} = \frac{\mu_P \, \Delta t \ln(2)}{2\sigma_P}. \qquad \text{(C37)}$$

References to Above:

[B1] I. N Levine, "Physical Chemistry," McGraw-Hill (New York), pp. 498-501 (1978).

[B2] F. Daniels, et al., "Experimental Physical Chemistry", McGraw Hill (New York), p.131 (1962).

Kinetics Calculations

Only two values of the parent concentration were recorded; P_0 and P_1 which reflect before and after the exposure period of length $(t_1 - t_0)$. In this case, no least squares regression is possible to determine the rate k_P in Equation C8:

$$k_P t = -\ln\left(\frac{P}{P_0}\right) \qquad \text{(A)}$$

In this circumstance, the only available estimate is

$$k_P = -\frac{1}{t_1 - t_0}\ln\left(\frac{P_1}{P_0}\right) = -\frac{1}{70.15 \text{ hrs}}\ln\left(\frac{59.5 \text{ ng/ml}}{88.1 \text{ ng/ml}}\right) = 0.0559 \text{ hr}^{-1}. \qquad \text{(B)}$$

The rate of photolysis in the reactor k_P is related to the actinic rate of photolysis k_{ACT} by

$$k_{ACT} = k_P\left(\frac{I_{ACT}}{I_R}\right) \qquad \text{(C)}$$

where I_{ACT} = 261 w/m^2 is the actinic solar intensity (at 45° south latitude) and the measured reactor intensity is I_R = 680 w/m^2. This gives

$$k_{ACT} = 0.0559\ hr^{-1}\left(\frac{261\ w/m^2}{680\ w/m^2}\right) = 0.00215\ hr^{-1} \qquad (D)$$

For samples under constant illumination, the reaction rate and half-life are related by Equation C9:

$$T^{1/2}_{p} = \frac{\ln(2)}{k_P} \qquad (E)$$

However, the actinic half-life is three times larger, according the standard eight-hour exposure day. This leads to

$$\text{(indirect photolysis) } T^{1/2}_{ACT} = \frac{3\ln(2)}{k_{ACT}} = 969\ hrs = 40.4\ days \qquad (F)$$

Appendix D: Individual Sample Data

This appendix includes individual sample data, quality control data and a table summarizing which samples failed to meet the quality control parameters.

Samples, Blanks and Standards from the LC/MS portion of the investigation that did not meet Data Quality Objectives.

Sample ID.	Description	Failed Criteria	Analyte	Value	Comments
EtFOSE-OH photolysis in Soils					
99039-267-01	3ppb std	75 -125% accuracy	EtFOSA	137%	failed 1/6 total 3ppb stds
032200-MC-44	Matrix Spike	75 -125% recovery	PFOA	37%	failed 2/5 analytes spiked
		75 -125% recovery	EtFOSE-OH	26%	
032200-MC-50	No Soil Spike	75 -125% recovery	PFOA	14%	failed 4/5 analytes spiked
			FOSA	15%	
			EtFOSA	127%	
			EtFOSE-OH	150%	
032200-MC-04	Matrix Spike	75 -125% recovery	EtFOSE-OH	48%	failed 1/5 analytes spiked
032200-MC-10	No Soil Spike	75 -125% recovery	EtFOSE-OH	-79%	failed 1/5 analytes spiked
032200-ST-44	Matrix Spike	75 -125% recovery	FOSA	132%	failed 3/5 analytes spiked
			EtFOSA	52%	
			EtFOSE-OH	-81%	
032200-ST-50	No Soil Spike	75 -125% recovery	EtFOSA	166%	failed 1/5 analytes spiked
032200-ST-24	Matrix Spike	75 -125% recovery	EtFOSE-OH	329%	failed 1/5 analytes spiked
032200-ST-04	Matrix Spike	75 -125% recovery	EtFOSE-OH	3%	failed 1/5 analytes spiked
032200-ST-10	No Soil Spike	75 -125% recovery	EtFOSE-OH	0%	failed 1/5 analytes spiked
032200-EPA-44	Matrix Spike	75 -125% recovery	EtFOSA	61%	failed 2/5 analytes spiked
			EtFOSE-OH	-4%	
032200-EPA-50	No Soil Spike	75 -125% recovery	PFOA	69%	failed 3/5 analytes spiked
			FOSA	36%	
			EtFOSE-OH	41%	
032200-EPA-24	Matrix Spike	75 -125% recovery	EtFOSE-OH	133%	failed 1/5 analytes spiked
032200-EPA-10	No Soil Spike	75 -125% recovery	EtFOSE-OH	288%	failed 1/5 analytes spiked
032200-EPA-30	No Soil Spike	75 -125% recovery	EtFOSE-OH	158%	failed 1/5 analytes spiked

Samples, Blanks and Standards from the LC/MS portion of the investigation that did not meet Data Quality Objectives (continued).

EtFOSE-OH photolysis in Fe_2O_3					
LC/MS					
0508-EtFOSFe-10	Control Spike	75 -125% recovery	EtFOSE-OH	13%	failed 1/5 analytes spiked
0508-EtFOSFe-16	Matrix Spike	75 -125% recovery	EtFOSE-OH	52%	failed 1/5 analytes spiked
0508-EtFOSFe-50	Control Spike	75 -125% recovery	EtFOSE-OH	138%	failed 1/5 analytes spiked
0508-EtFOSFe-56	Matrix Spike	75 -125% recovery	EtFOSE-OH	126%	failed 1/5 analytes spiked
GC/MS					
0508-EtFOSFe-96	Control Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	13.64ppb	Data questionable. Retention time change due to organic solvent in samples.
0508-EtFOSFe-91	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	11.21ppb	
0508-EtFOSFe-102	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	12.53ppb	
0508-EtFOSFe-106	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	14.76ppb	
0508-EtFOSFe-107	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	12.36ppb	
0508-EtFOSFe-61	Matrix Blank	Detected; LOQ (12ppb)	1H-perfluoropropane	16.07ppb	
0508-EtFOSFe-62	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	16.07ppb	
0508-EtFOSFe-66	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	13.32ppb	
0508-EtFOSFe-72	Matrix Spike	Detected; LOQ (12ppb)	1H-perfluoropropane	14.44ppb	
0508-EtFOSFe-66	Matrix Spike	75 -125% recovery	1H-perfluoroheptane	133%	failed 1/8 analytes spiked
0508-EtFOSFe-67	Matrix Spike	75 -125% recovery	1H-perfluoroheptane	146%	failed 2/8 analytes spiked
0508-EtFOSFe-67			1H-perfluorohexane	126%	
0508-EtFOSFe-70	Control Spike	75 -125% recovery	1H-perfluorooctane	66%	failed 1/8 analytes spiked
0508-EtFOSEfe-71 through 96		75-125% recovery	see data sheet	0-OK	failed multiple analytes spiked
0508-EtFOSFe-99	Matrix Spike	75 -125% recovery	see data sheet	146%	failed 7/8 analytes spiked
0508-EtFOSEfe100	Control Spike	75-125% recovery	see data sheet	64,61	failed 6/8 analytes spiked
0508-EtFOSEfe116	Matrix Spike	75-125% recovery	1H-C_8, 2H-C_8	64,61	failed 2/8 analytes spiked
0508-EtFOSEfe117	Matrix Spike	75-125% recovery	1H-C_8, 2H-C_8	55,55	failed 2/8 analytes spiked

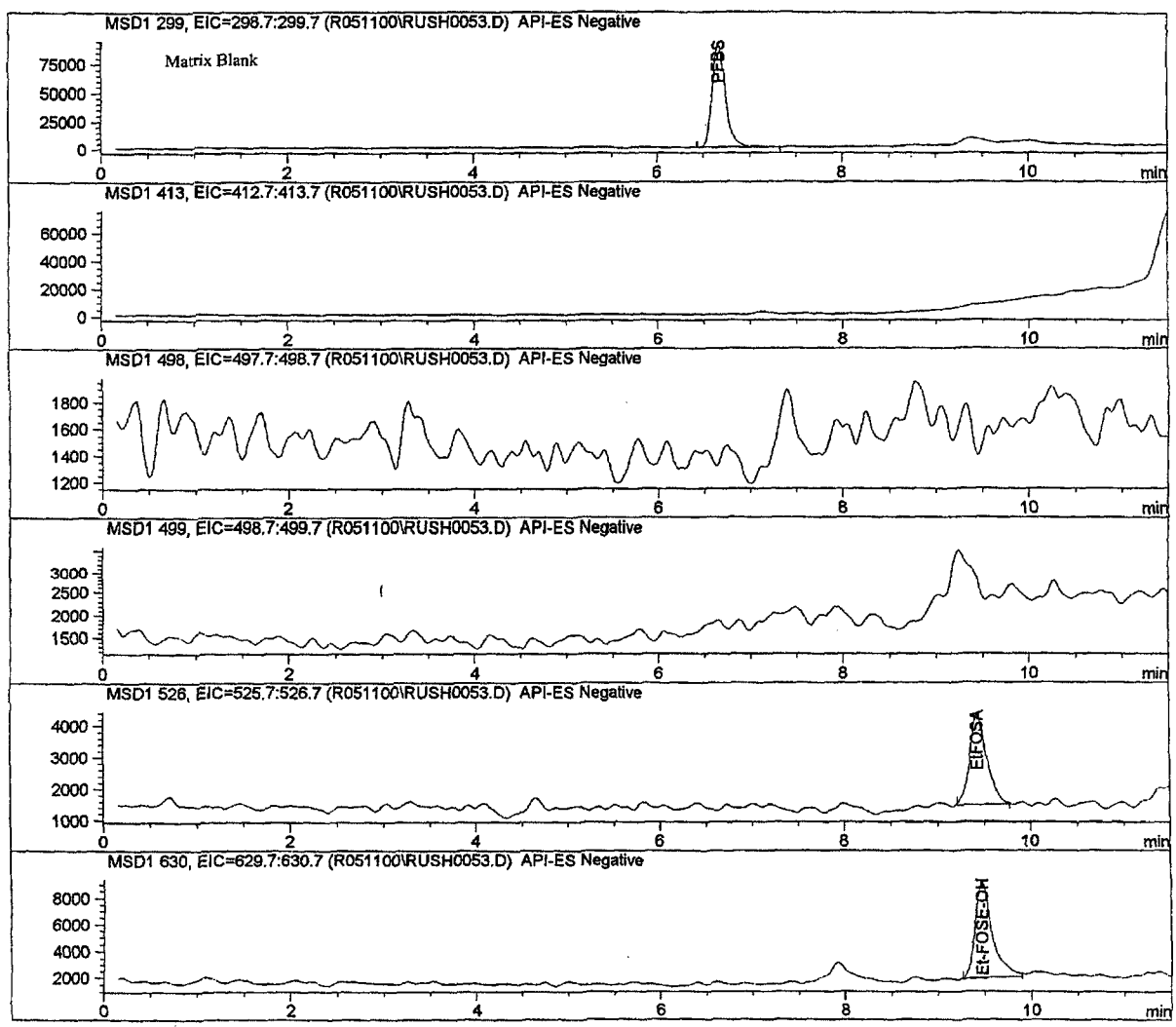
Appendix E: Representative Chromatograms

Chromatograms from the present study are included in this appendix.

tch Run # 53 of 62
ta File C:\HPCHEM\1\DATA\R051100\rush0053.D Sample Name: 00028-32-00

Injection Date	: 5/12/00 11:28:33 AM	Seq. Line :	53
Sample Name	: 00028-32-00	Vial :	1
Acq. Operator	: kej	Inj :	1
Acq. Instrument	: Rush	Inj Volume :	5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej		
	(modified after loading)		

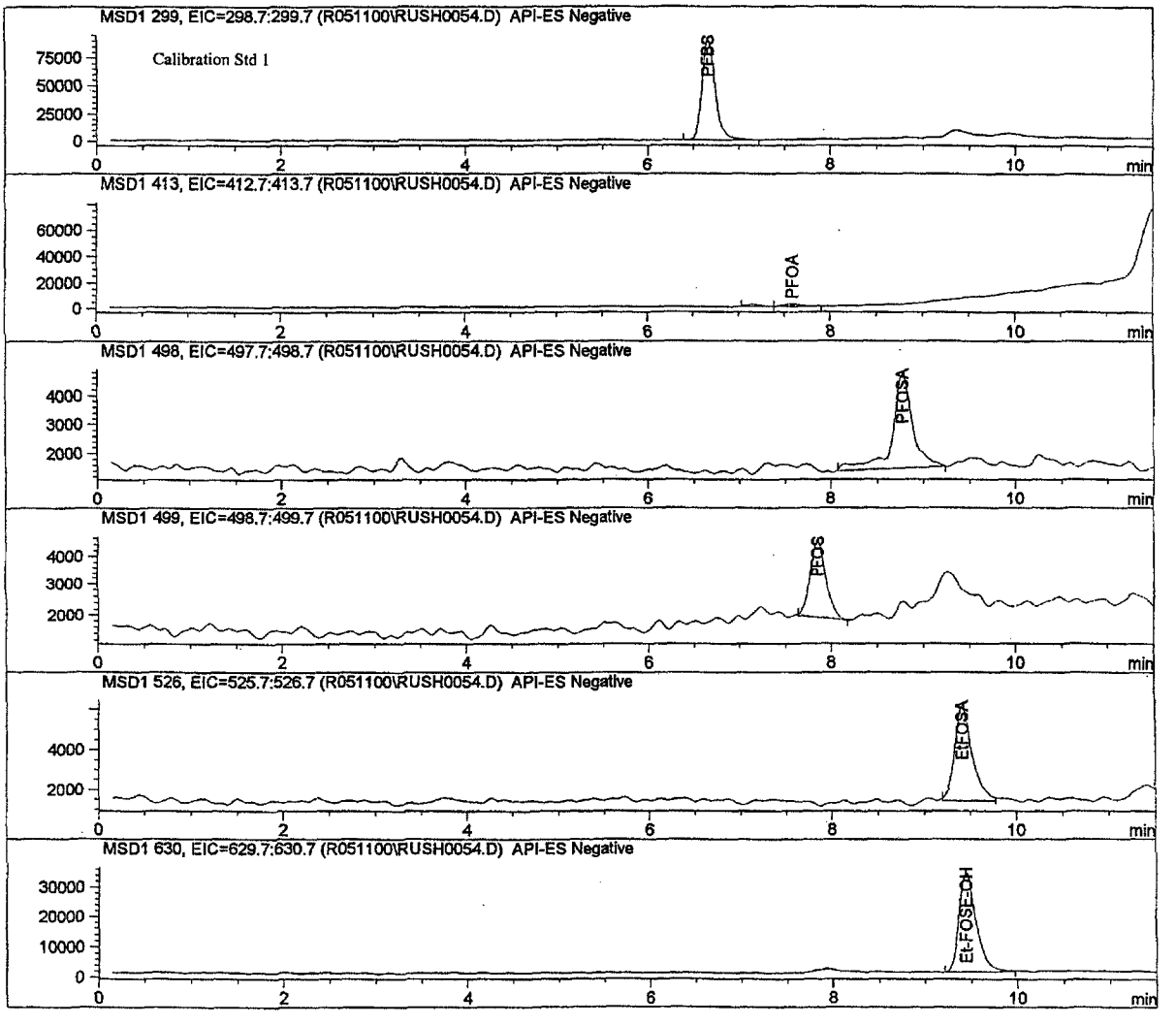
SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



tch Run # 54 of 62
ta File C:\HPCHEM\1\DATA\R051100\rush0054.D Sample Name: 00028-32-01

Injection Date	: 5/12/00 11:47:59 AM	Seq. Line	: 54
Sample Name	: 00028-32-01	Vial	: 2
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

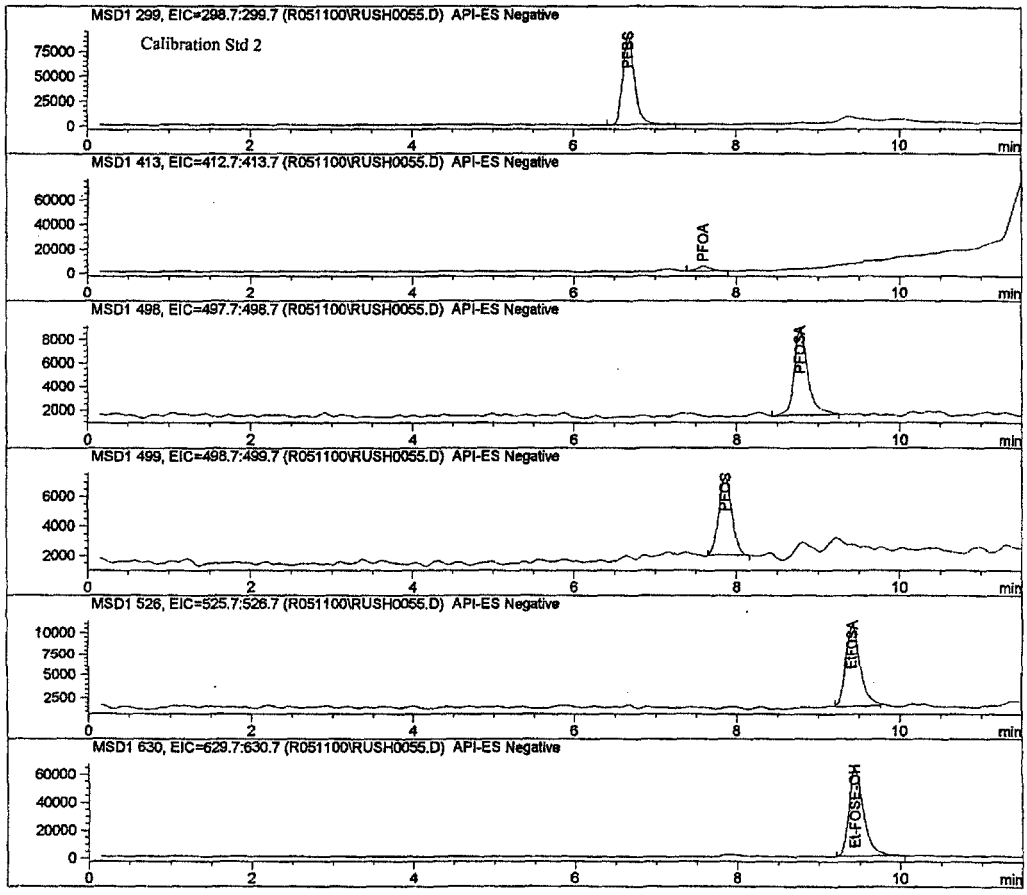
SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



Batch Run # 55 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0055.D Sample Name: 00028-32-02

Injection Date	: 5/12/00 12:07:21 PM	Seq. Line	: 55
Sample Name	: 00028-32-02	Vial	: 3
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

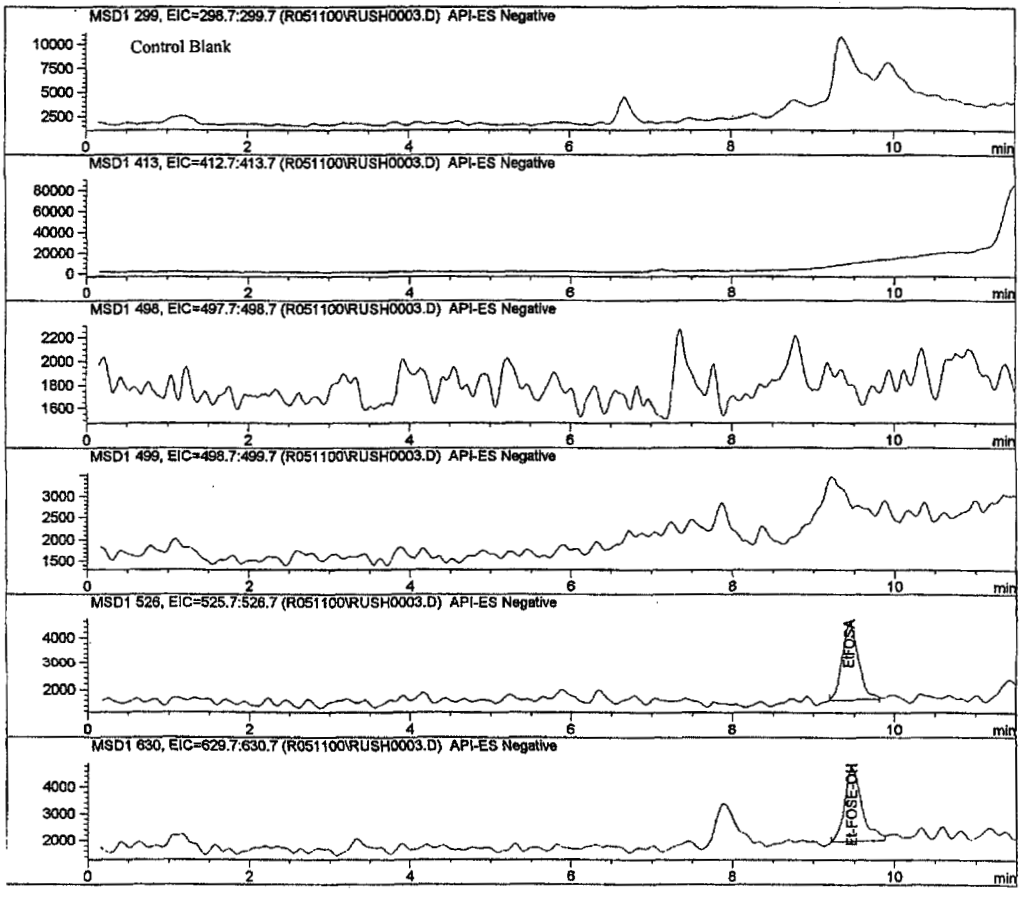


Instrument 1 5/24/00 12:46:55 PM kej Page 1 of 2

Batch Run # 3 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0003.D Sample Name: 1:7 MilliQ/MeOH

Injection Date	: 5/11/00 7:24:17 PM	Seq. Line	: 3
Sample Name	: 1:7 MilliQ/MeOH	Vial	: 98
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

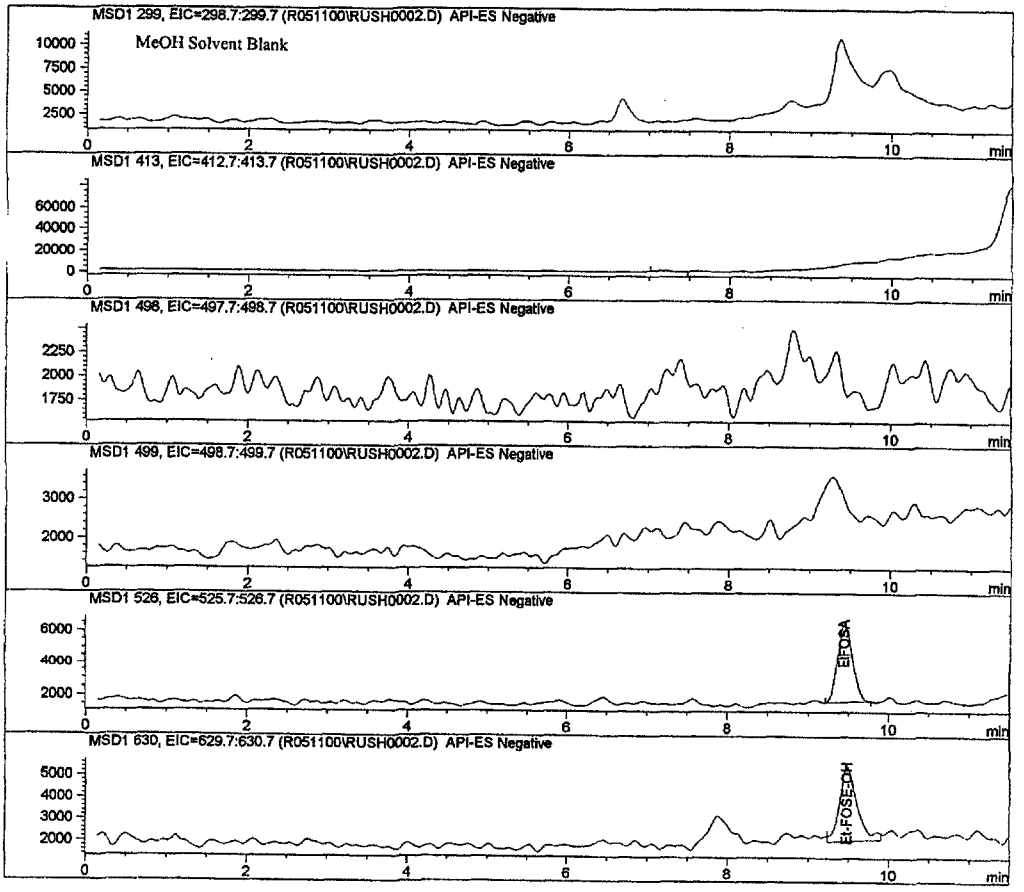


Instrument 1 5/24/00 12:43:06 PM kej Page 1 of 2

Batch Run # 2 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0002.D Sample Name: MeOH blank

Injection Date	: 5/11/00 7:04:58 PM	Seq. Line :	2
Sample Name	: MeOH blank	Vial :	99
Acq. Operator	: kej	Inj :	1
Acq. Instrument	: Rush		
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej		

(modified after loading) (Results are from a previously saved SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



Instrument 1 5/24/00 12:43:01 PM kej

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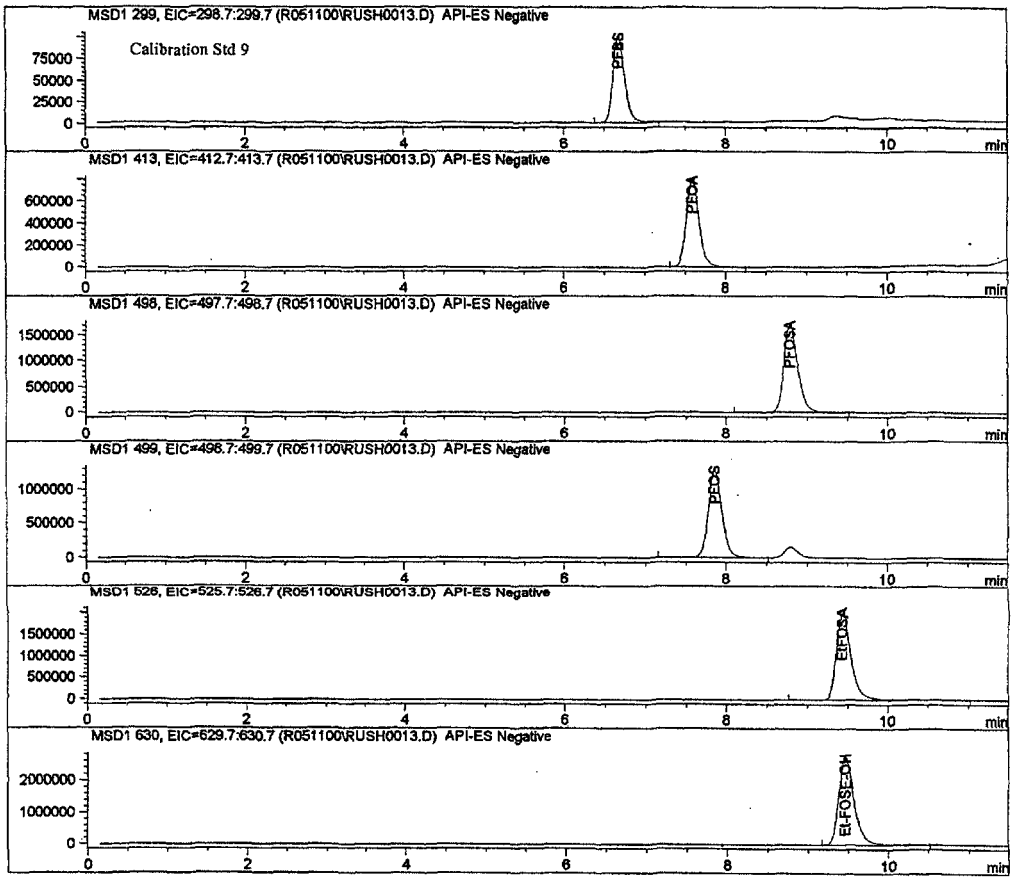
Batch Run # 13 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0013.D Sample Name: 00028-32-09

Injection Date	: 5/11/00 10:37:01 PM	Seq. Line	: 13
Sample Name	: 00028-32-09	Vial	: 10
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



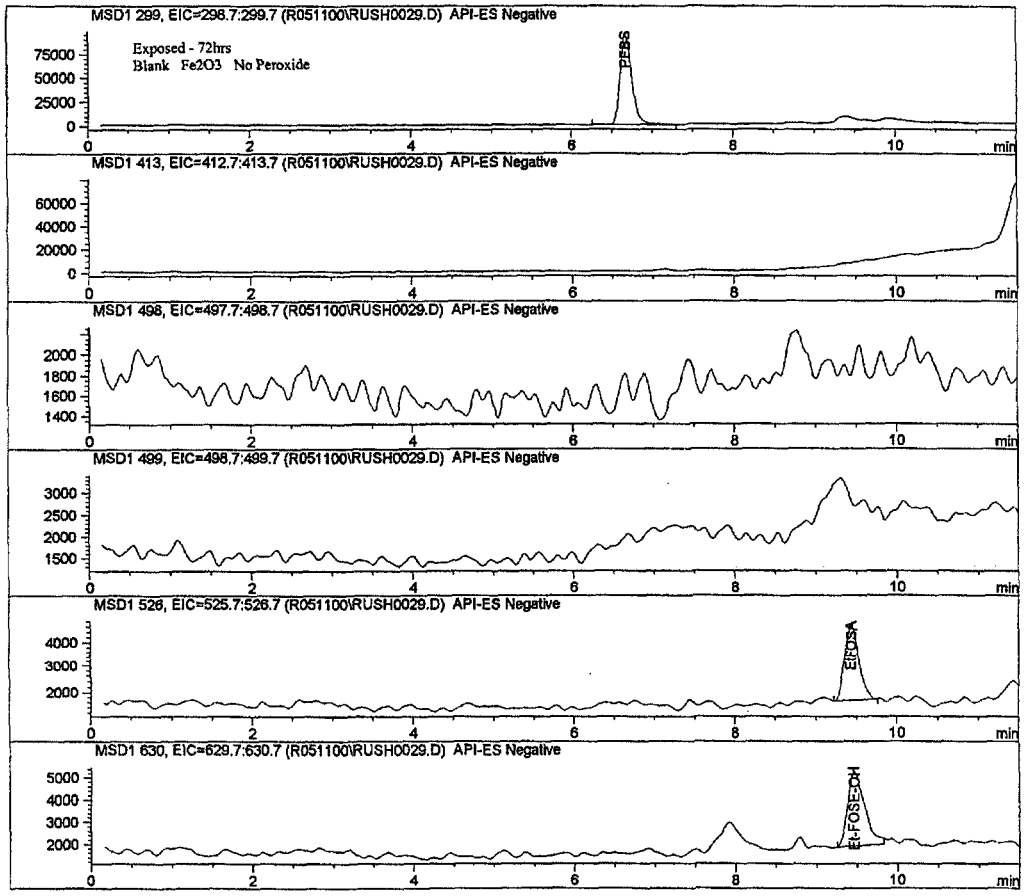
Instrument 1 5/24/00 12:43:50 PM kej

Page 1 of 2

Batch Run # 29 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0029.D Sample Name: 0508-EtFOSfe-11

Injection Date	: 5/12/00 3:45:32 AM	Seq. Line :	29
Sample Name	: 0508-EtFOSfe-11	Vial :	21
Acq. Operator	: kej	Inj :	1
Acq. Instrument	: Rush	Inj Volume :	5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

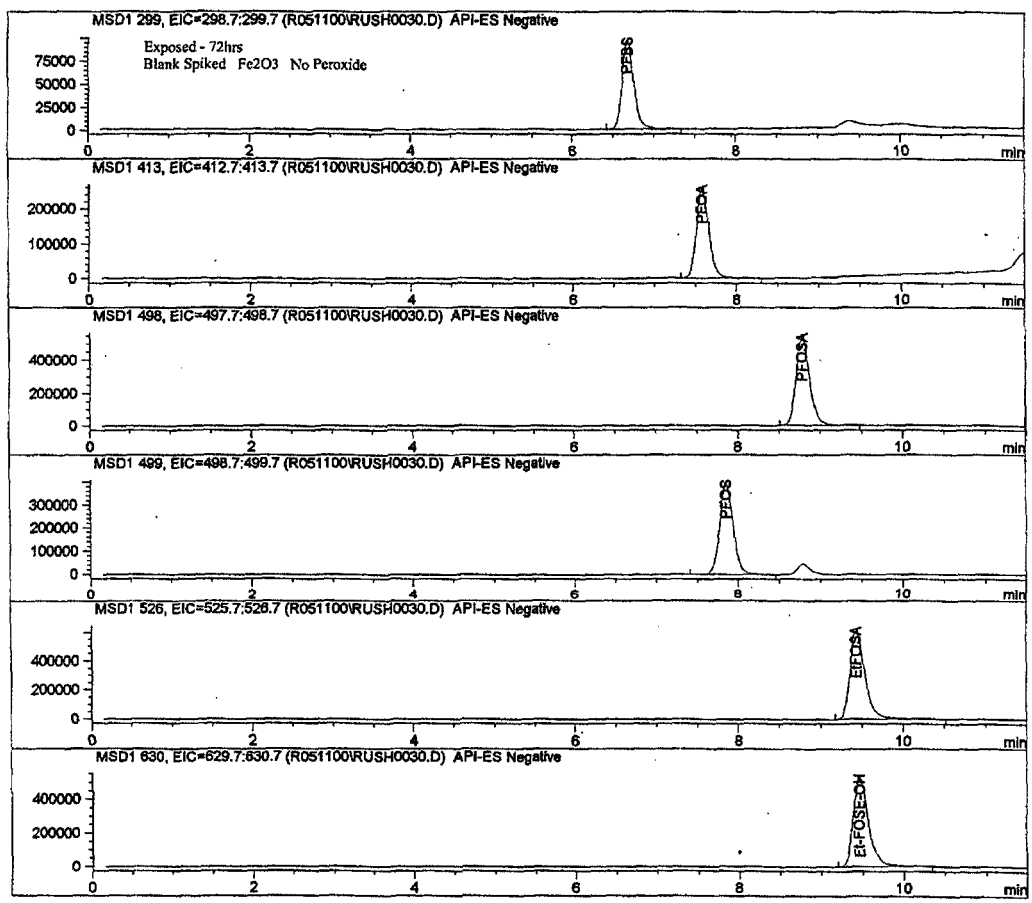


Instrument 1 5/24/00 12:45:01 PM kej Page 1 of 2

Batch Run # 30 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0030.D Sample Name: 0508-EtFOSfe-12

Injection Date	: 5/12/00 4:04:47 AM	Seq. Line	: 30
Sample Name	: 0508-EtFOSfe-12	Vial	: 22
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

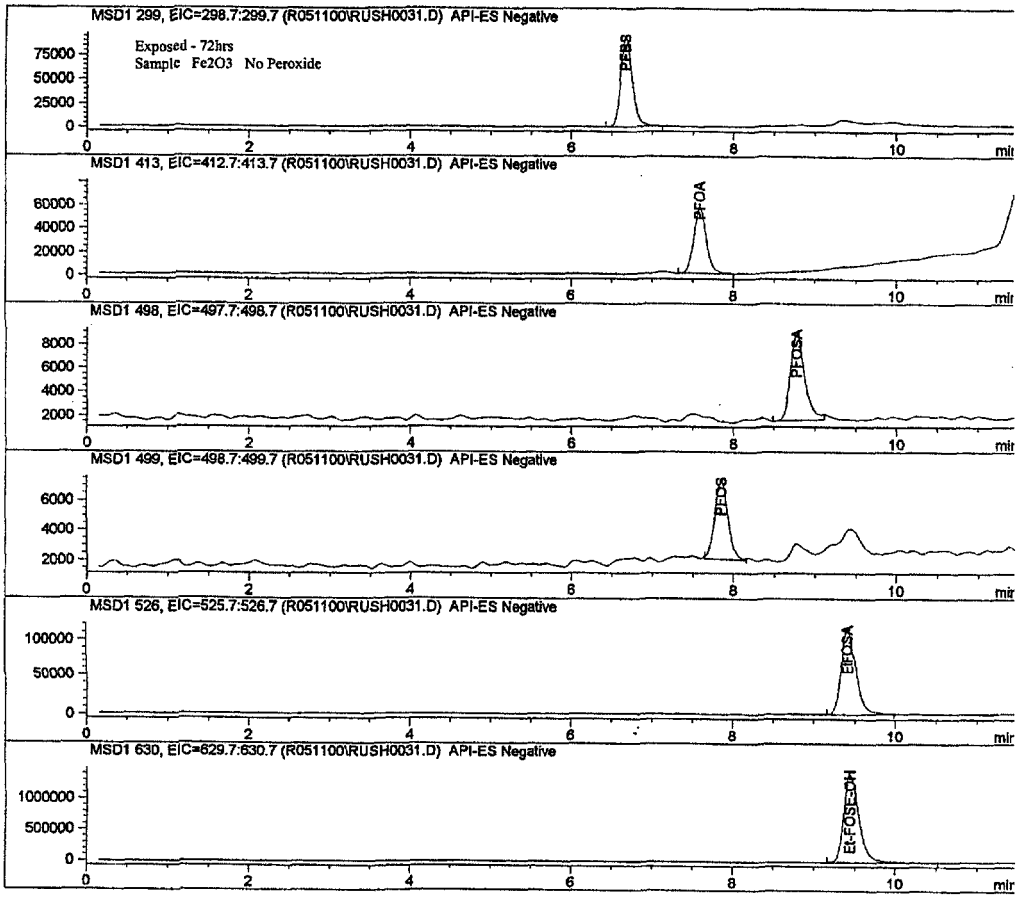


Instrument 1 5/24/00 12:45:05 PM kej Page 1 of 2

Batch Run # 31 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0031.D Sample Name: 0508-EtFOSfe-1:

Injection Date	: 5/12/00 4:24:02 AM	Seq. Line	: 31
Sample Name	: 0508-EtFOSfe-13	Vial	: 23
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



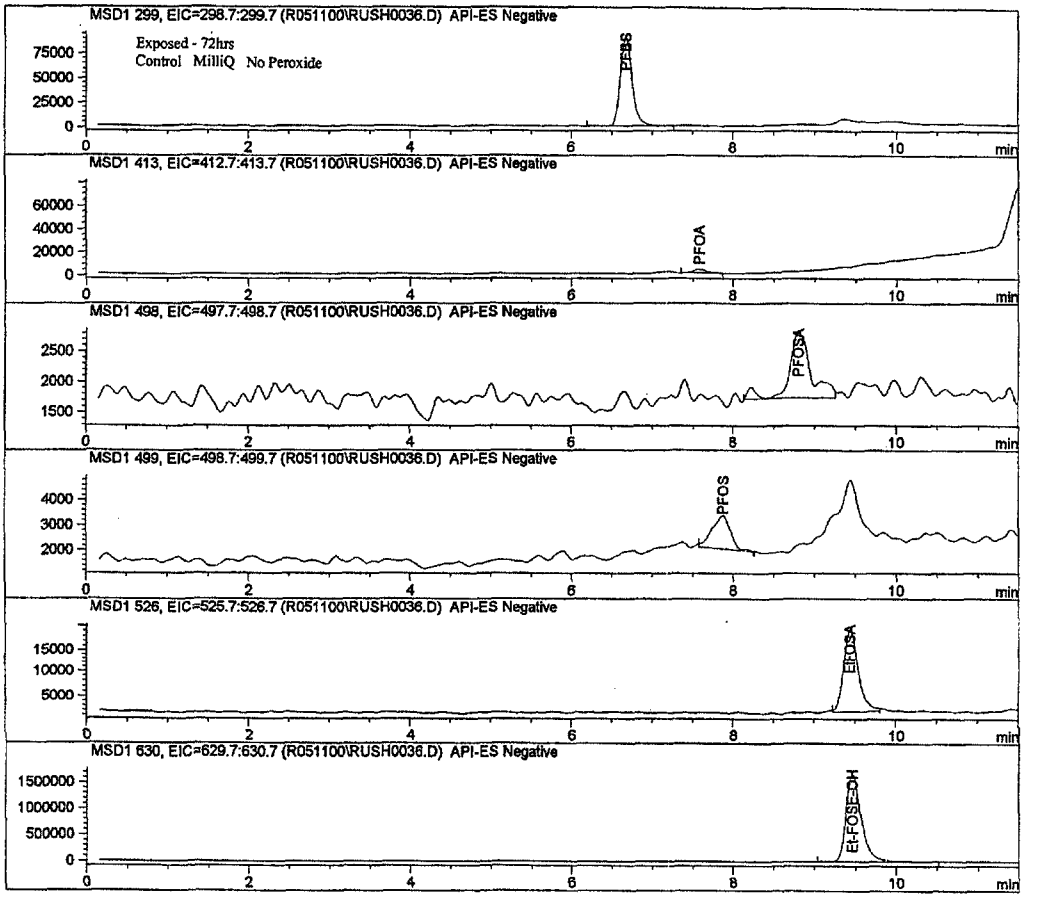
Instrument 1 5/24/00 12:45:09 PM kej

Page 1 of 2

Batch Run # 36 of 62
Data File C:\HPCHEM\1\DATA\R051100\rush0036.D Sample Name: 0508-EtFOSfe-18

Injection Date	: 5/12/00 6:00:26 AM	Seq. Line	: 36
Sample Name	: 0508-EtFOSfe-18	Vial	: 28
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511A1.M		
Last changed	: 5/24/00 12:42:54 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

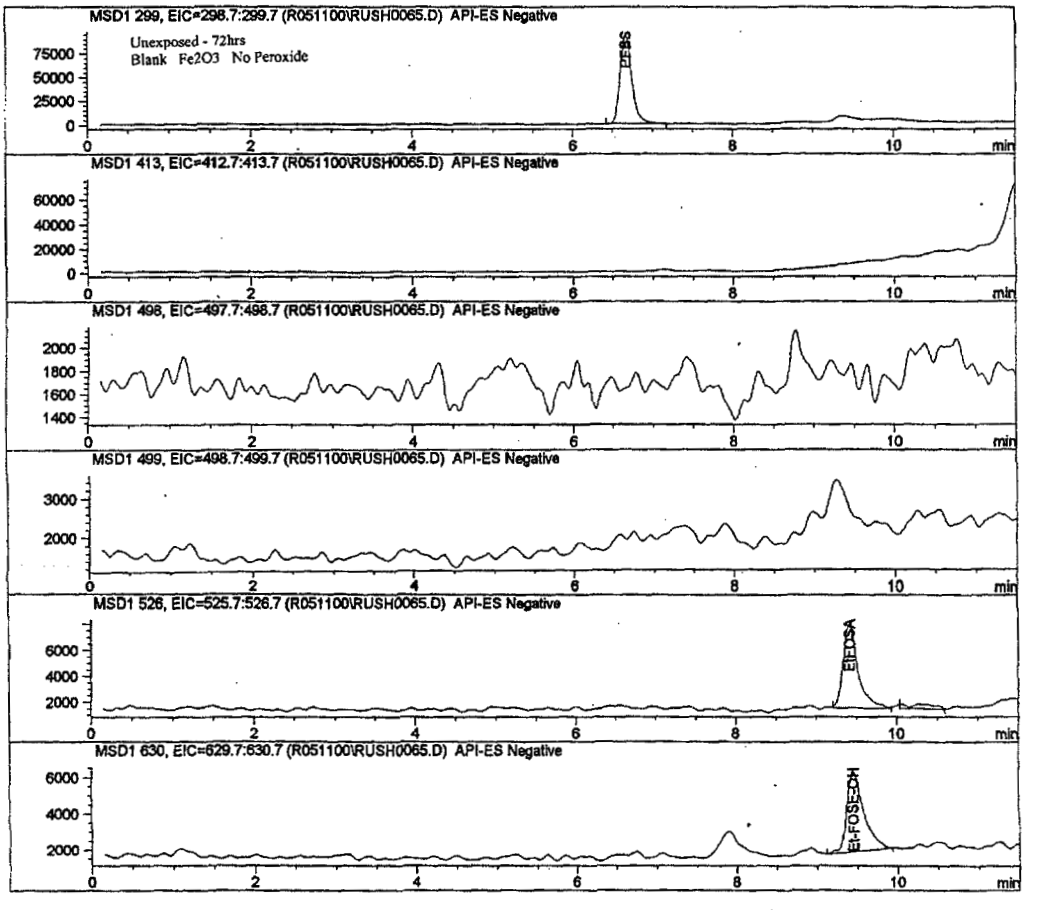


Instrument 1 5/24/00 12:45:32 PM kej Page 1 of 2

Batch Run # 14 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0065.D Sample Name: 0508-EtFOSfe-31

Injection Date	: 5/12/00 3:20:38 PM	Seq. Line	: 65
Sample Name	: 0508-EtFOSfe-31	Vial	: 41
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

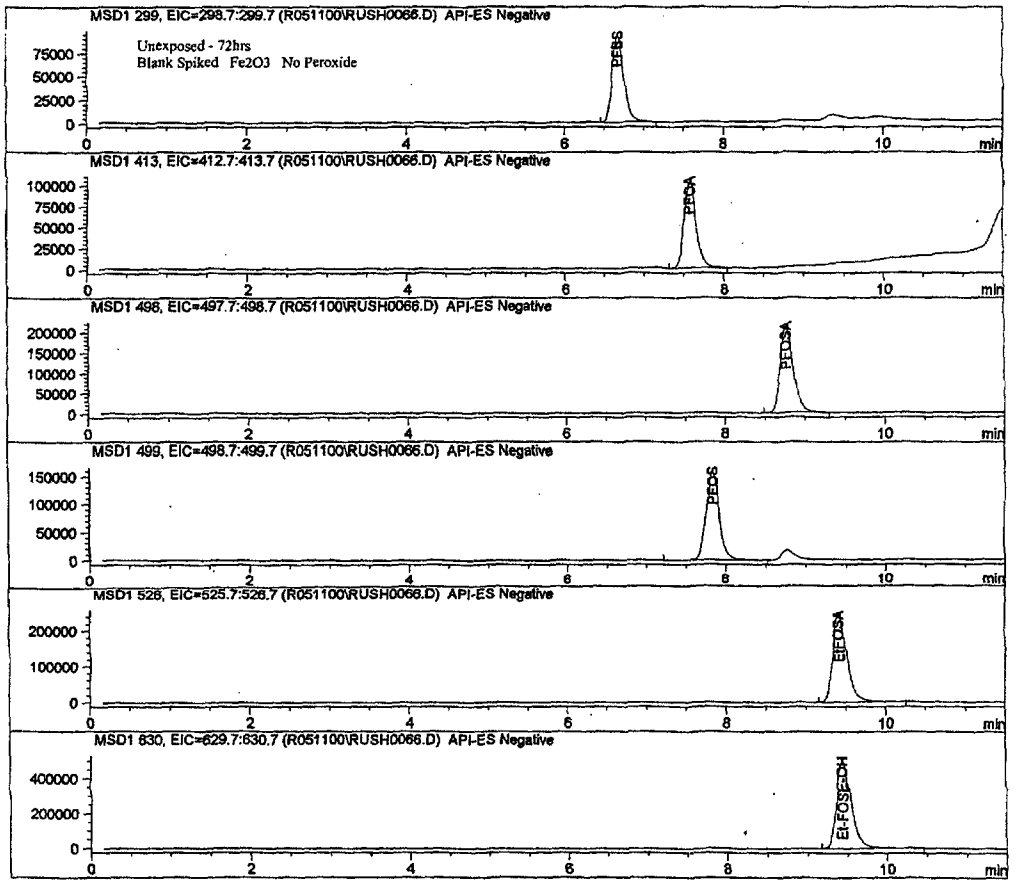


Instrument 1 5/24/00 2:15:52 PM kej Page 1 of 2

Batch Run # 15 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0066.D Sample Name: 0508-EtFOSfe-32

Injection Date	: 5/12/00 3:39:56 PM	Seq. Line	: 66
Sample Name	: 0508-EtFOSfe-32	Vial	: 42
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



Instrument 1 5/24/00 2:15:56 PM kej

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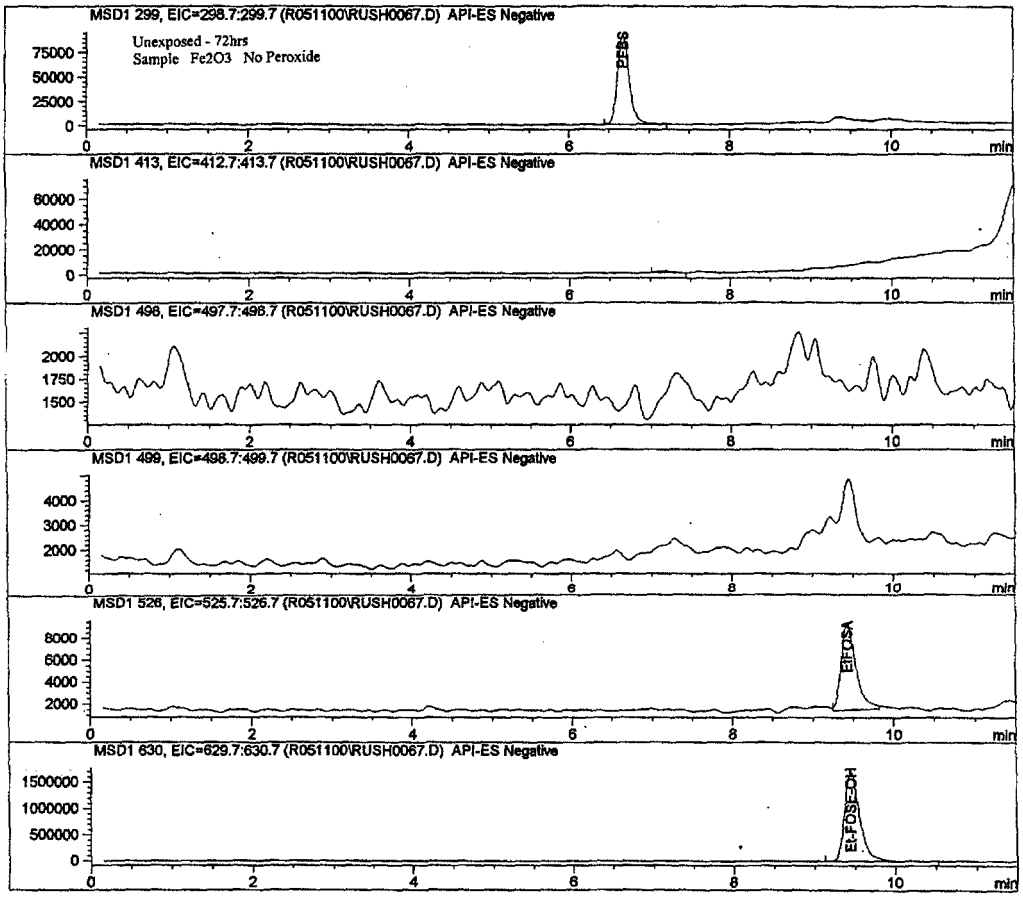
Batch Run # 16 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0067.D Sample Name: 0508-EtFOSfe-33

Injection Date	: 5/12/00 3:59:13 PM	Seq. Line	: 67
Sample Name	: 0508-EtFOSfe-33	Vial	: 43
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

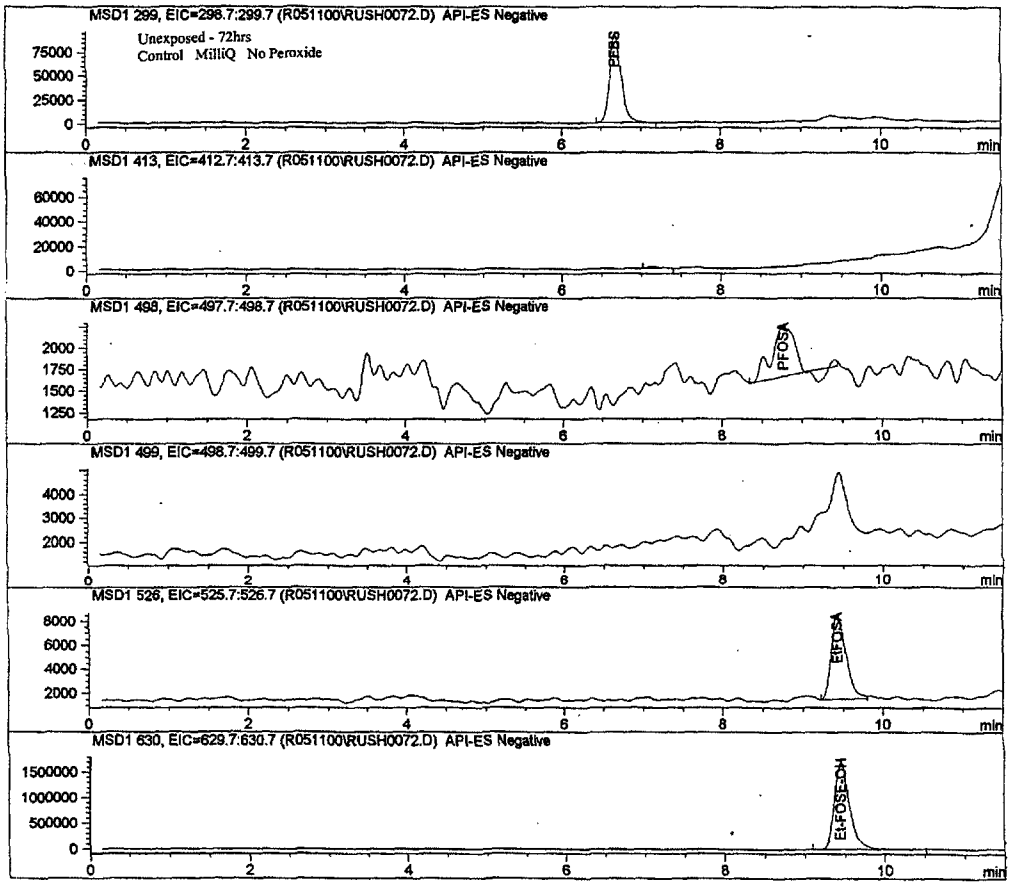


Instrument 1 5/24/00 2:16:01 PM kej Page 1 of 2

Batch Run # 21 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0072.D Sample Name: 0508-EtFOSfe-38

Injection Date	: 5/12/00 5:35:37 PM	Seq. Line	: 72
Sample Name	: 0508-EtFOSfe-38	Vial	: 48
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

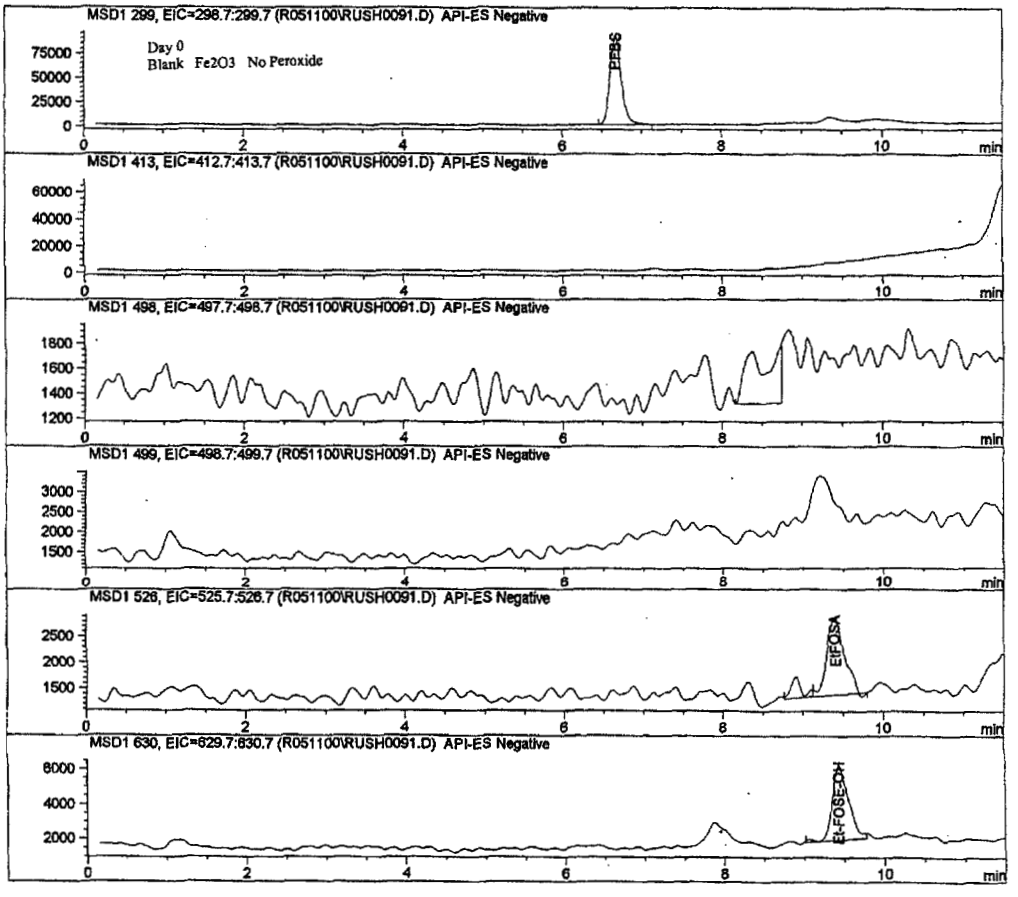
SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



Batch Run # 40 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0091.D Sample Name: 0508-EtFOSfe-51

Injection Date	: 5/12/00 11:42:33 PM	Seq. Line	: 91
Sample Name	: 0508-EtFOSfe-51	Vial	: 61
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

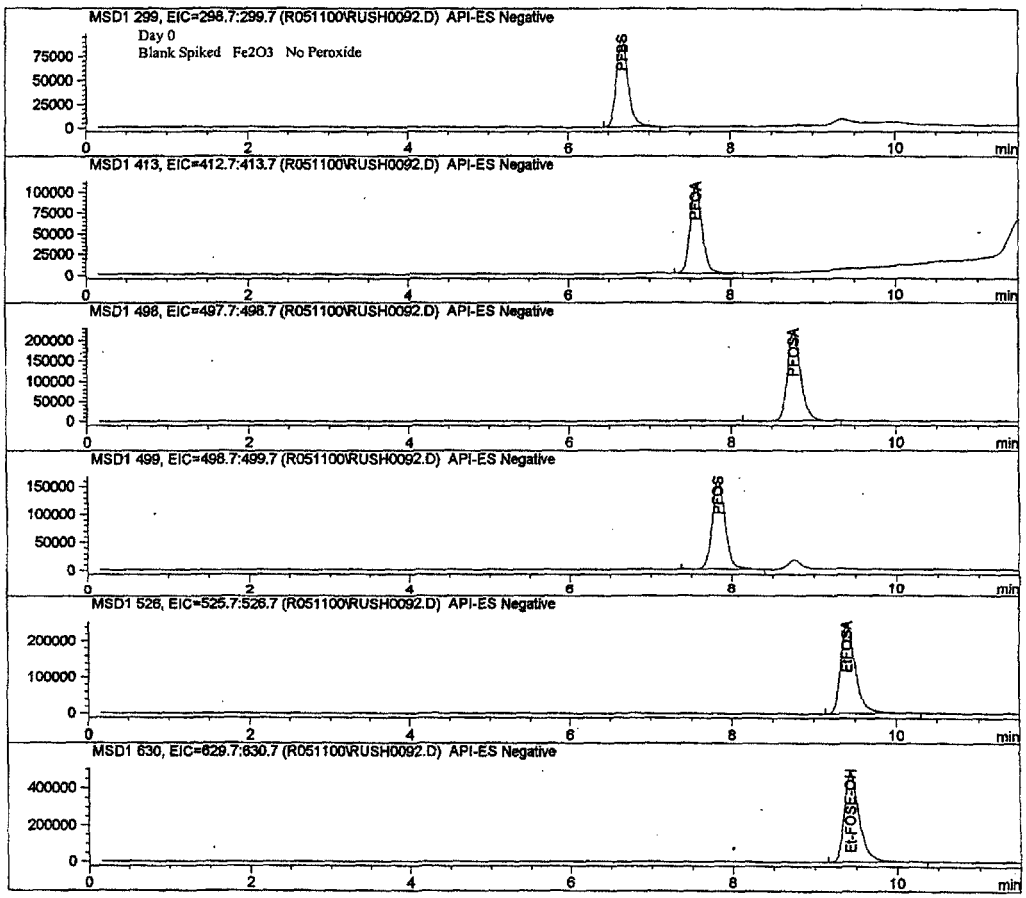


Instrument 1 5/24/00 2:17:49 PM kej Page 1 of 2

Batch Run # 41 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0092.D Sample Name: 0508-EtFOSfe-52

Injection Date	: 5/13/00 12:01:50 AM	Seq. Line	: 92
Sample Name	: 0508-EtFOSfe-52	Vial	: 62
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.

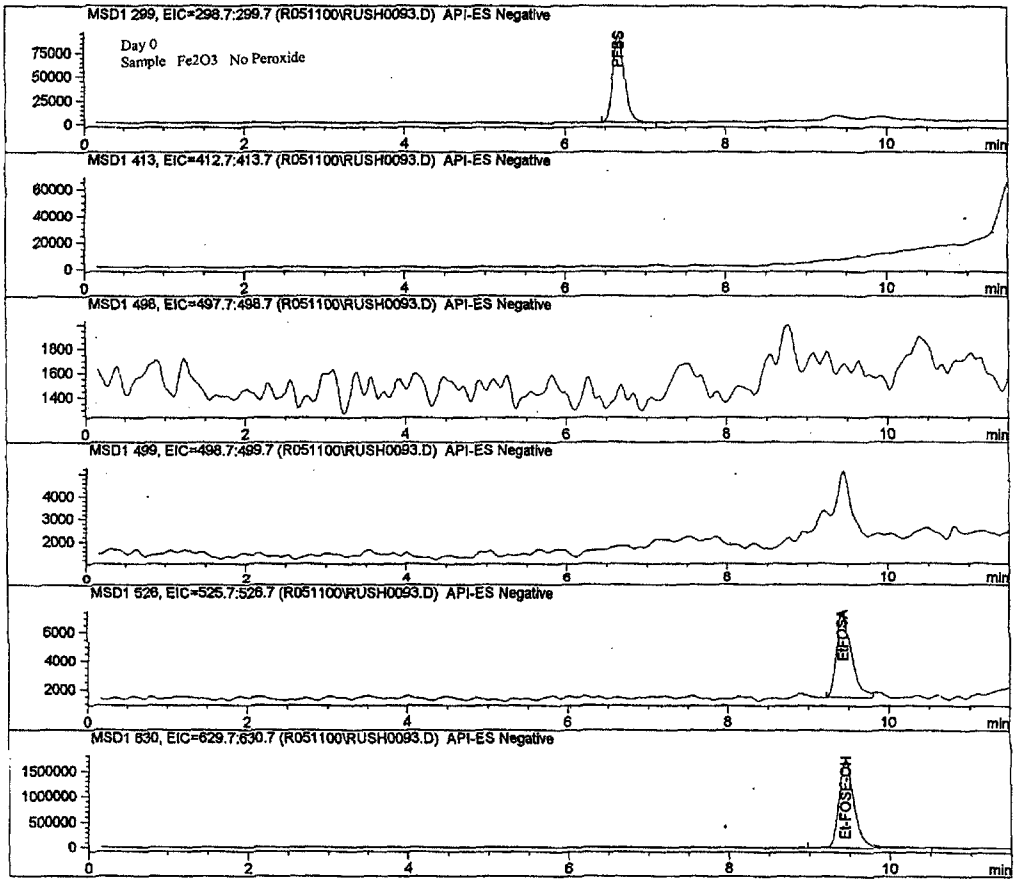


Instrument 1 5/24/00 2:17:54 PM kej Page 1 of 2

Batch Run # 42 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0093.D Sample Name: 0508-EtFOSfe-53

Injection Date	: 5/13/00 12:21:06 AM	Seq. Line :	93
Sample Name	: 0508-EtFOSfe-53	Vial :	63
Acq. Operator	: kej	Inj :	1
Acq. Instrument	: Rush	Inj Volume :	5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



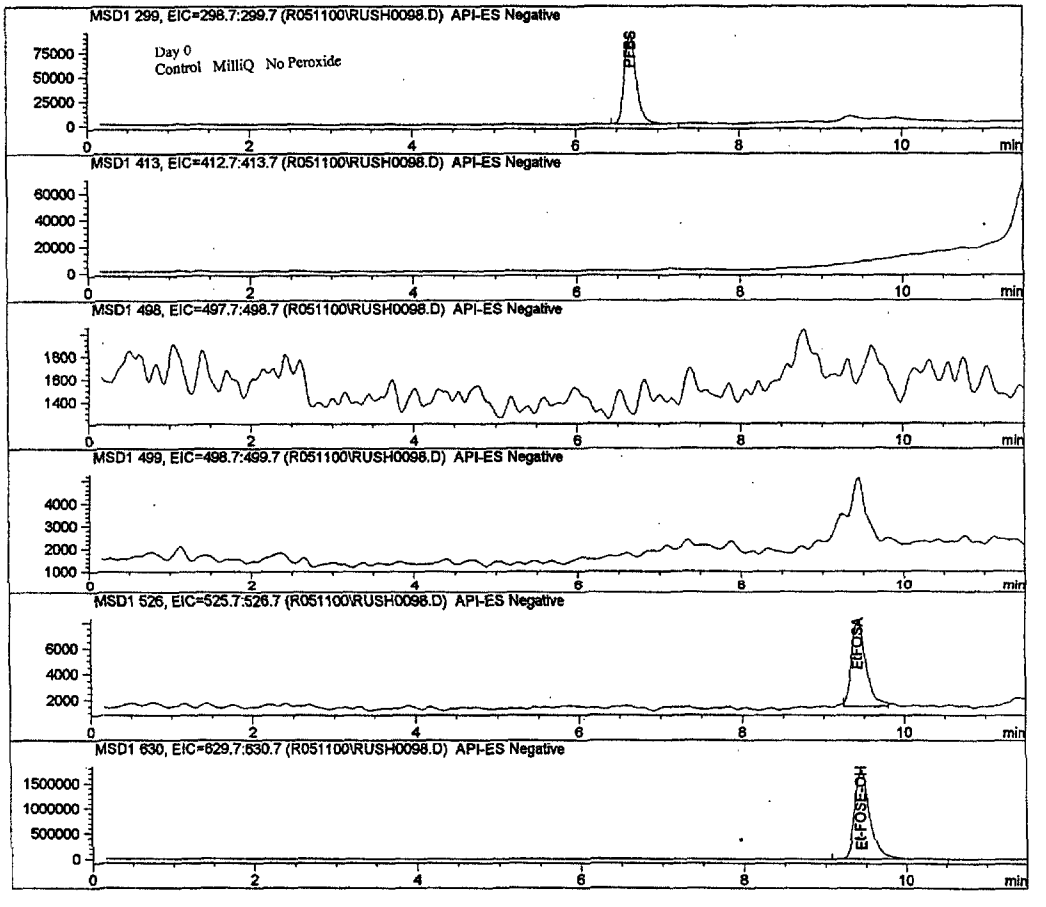
Instrument 1 5/24/00 2:17:58 PM kej

Page 1 of 2

Batch Run # 47 of 61
Data File C:\HPCHEM\1\DATA\R051100\rush0098.D Sample Name: 0508-EtFOSfe-58

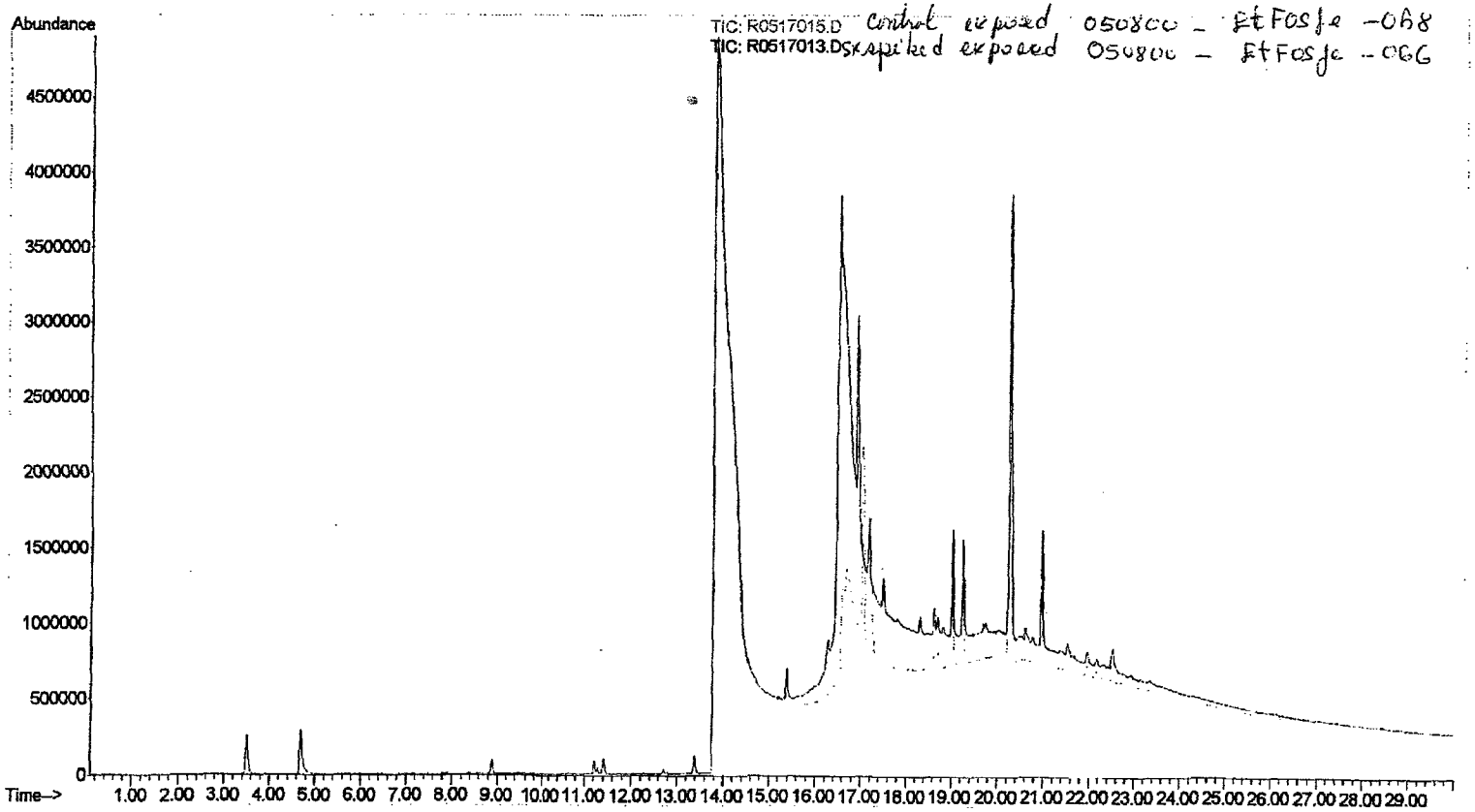
Injection Date	: 5/13/00 1:57:42 AM	Seq. Line	: 98
Sample Name	: 0508-EtFOSfe-58	Vial	: 68
Acq. Operator	: kej	Inj	: 1
Acq. Instrument	: Rush	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ETFO511.M		
Last changed	: 5/11/00 6:44:10 PM by kej		
Analysis Method	: C:\HPCHEM\1\METHODS\R0511B1.M		
Last changed	: 5/24/00 2:14:48 PM by kej (modified after loading)		

SIM Analysis (ES-) for PFOS/PFBS/PFOA using Dionex IonPac NG1 column, 4x35mm.



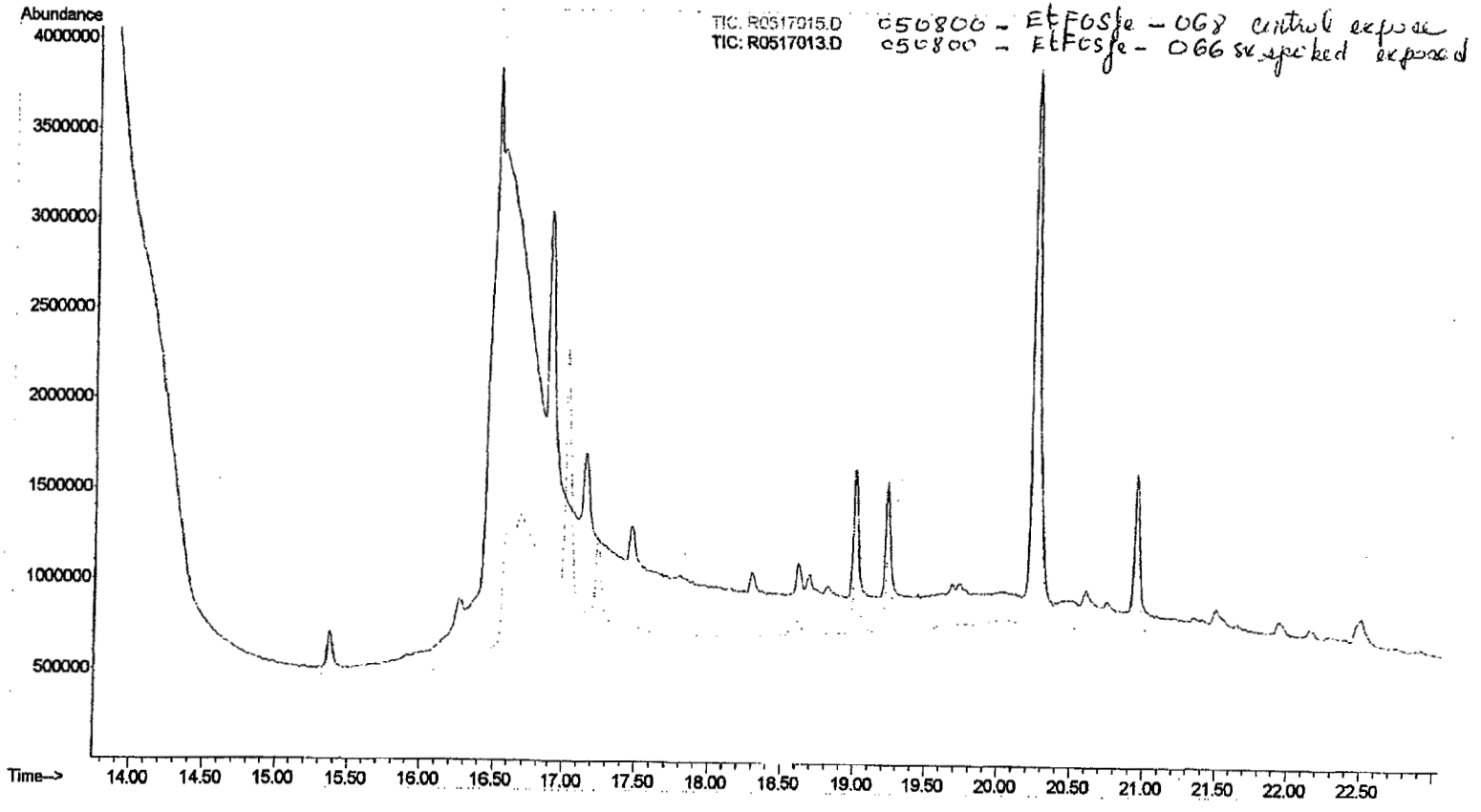
Instrument 1 5/24/00 2:18:21 PM kej Page 1 of 2

File : E:\R051700\R0517015.D
Operator : RM
Acquired : 17 May 2000 21:08 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-068 control exp
Misc Info :
Vial Number: 15



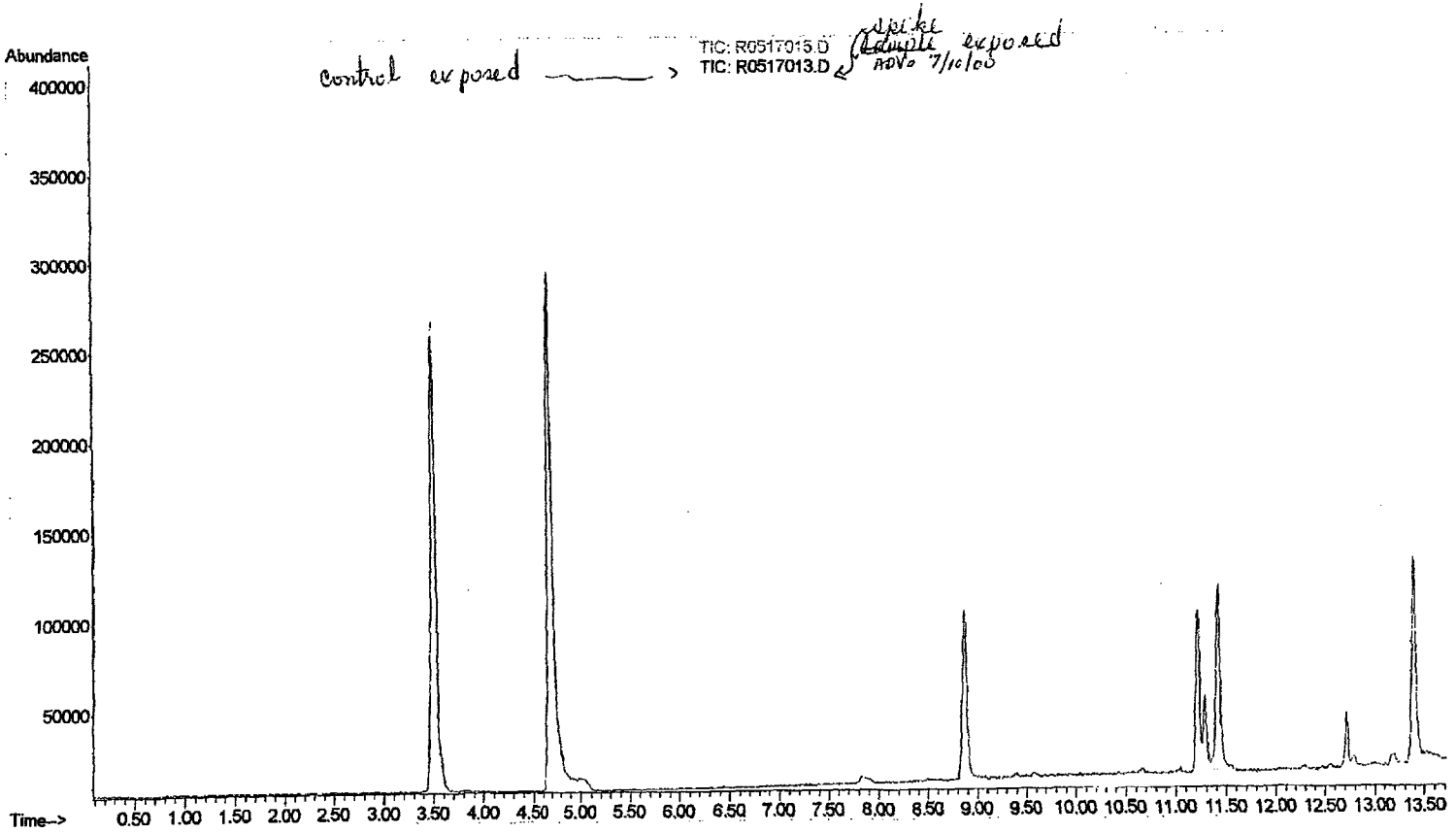
BACK TO MAIN

File : E:\R051700\R0517015.D
Operator : RM
Acquired : 17 May 2000 21:08 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-068 control exp
Misc Info :
Vial Number: 15



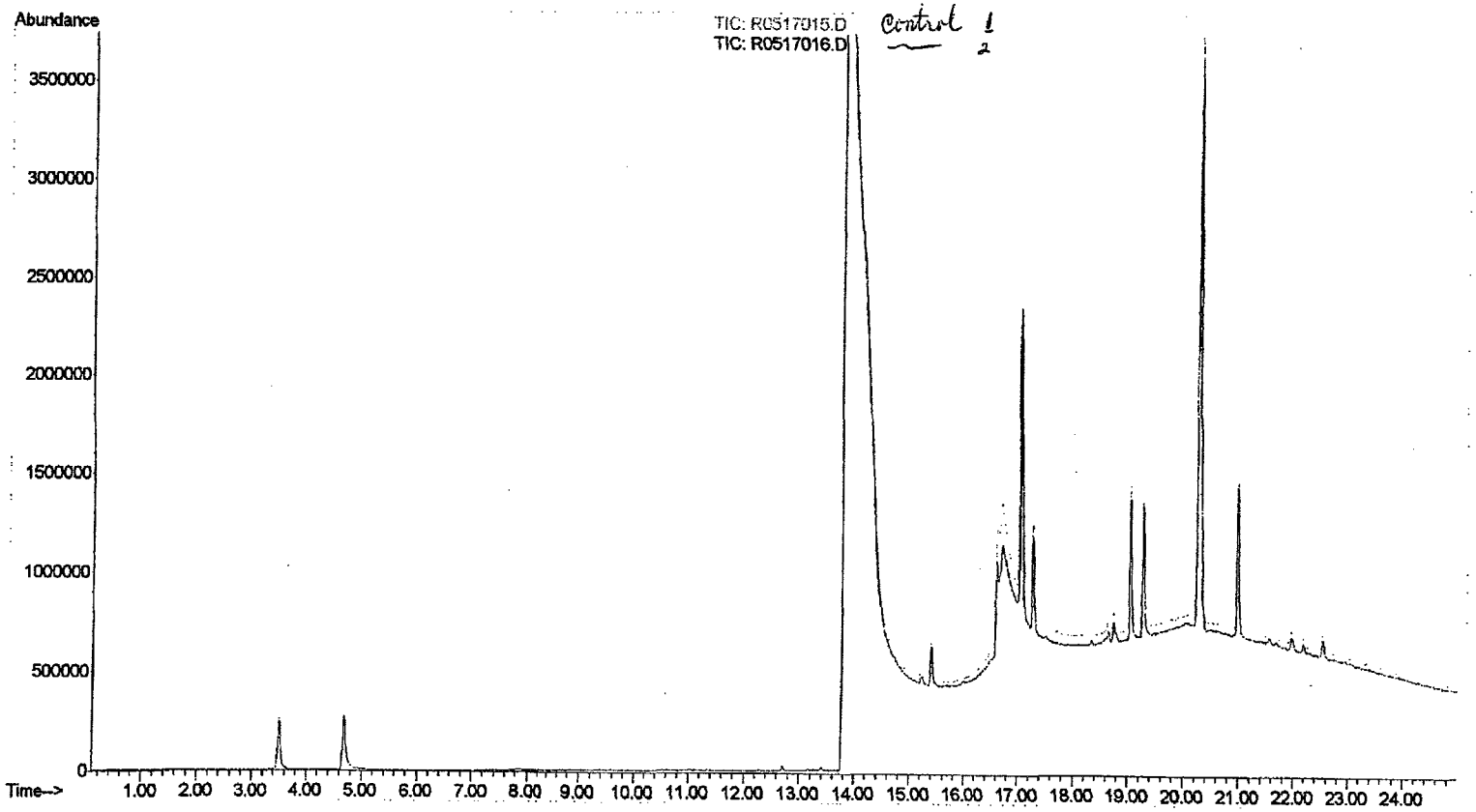
BACK TO MAIN

File : E:\R051700\R0517015.D
Operator : RM
Acquired : 17 May 2000 21:08 using AcqMethod VOA_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-068 control exp
Misc Info :
Vial Number: 15



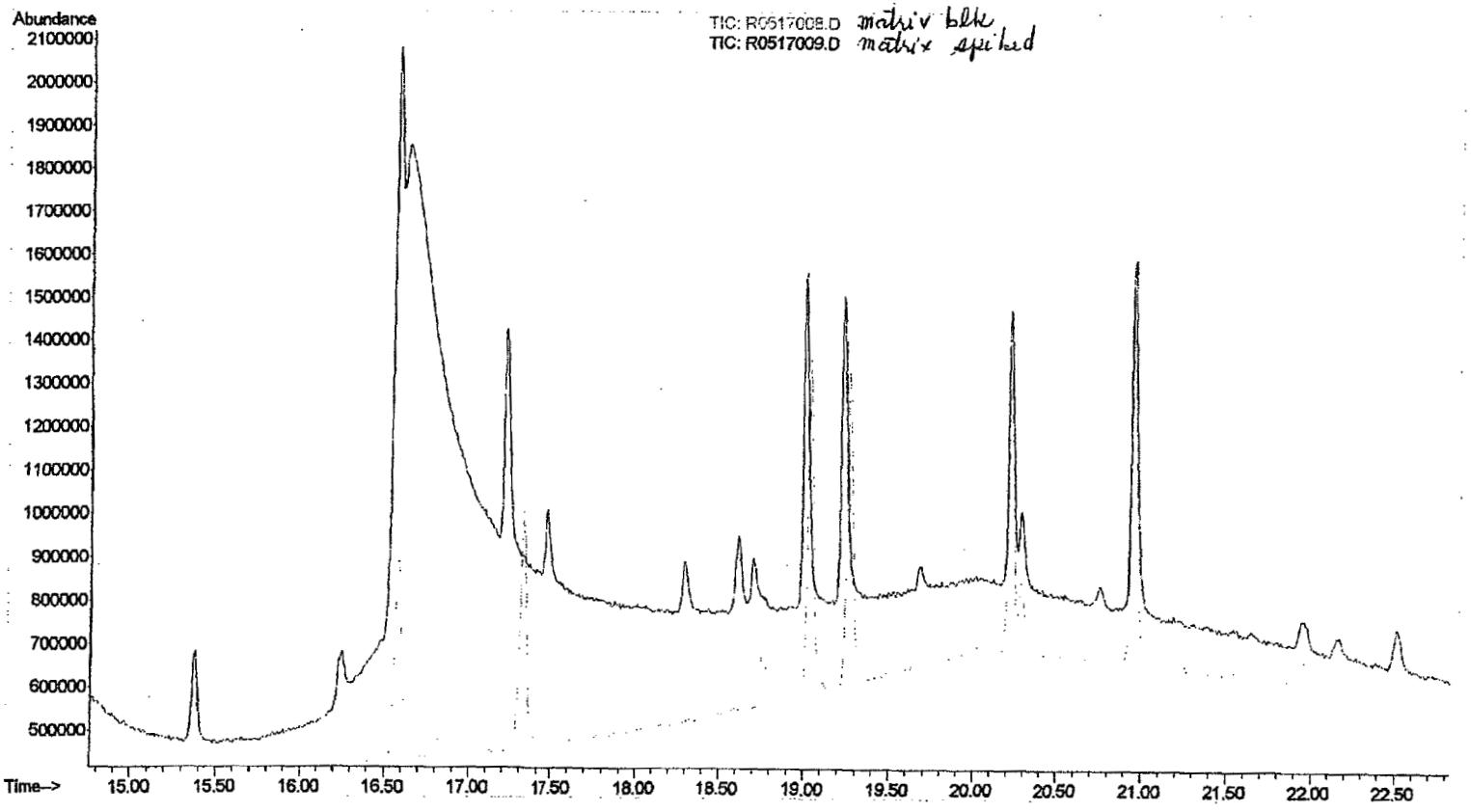
BACK TO MAIN

File : E:\R051700\R0517015.D
Operator : RM
Acquired : 17 May 2000 21:08 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-068 control exp
Misc Info :
Vial Number: 15



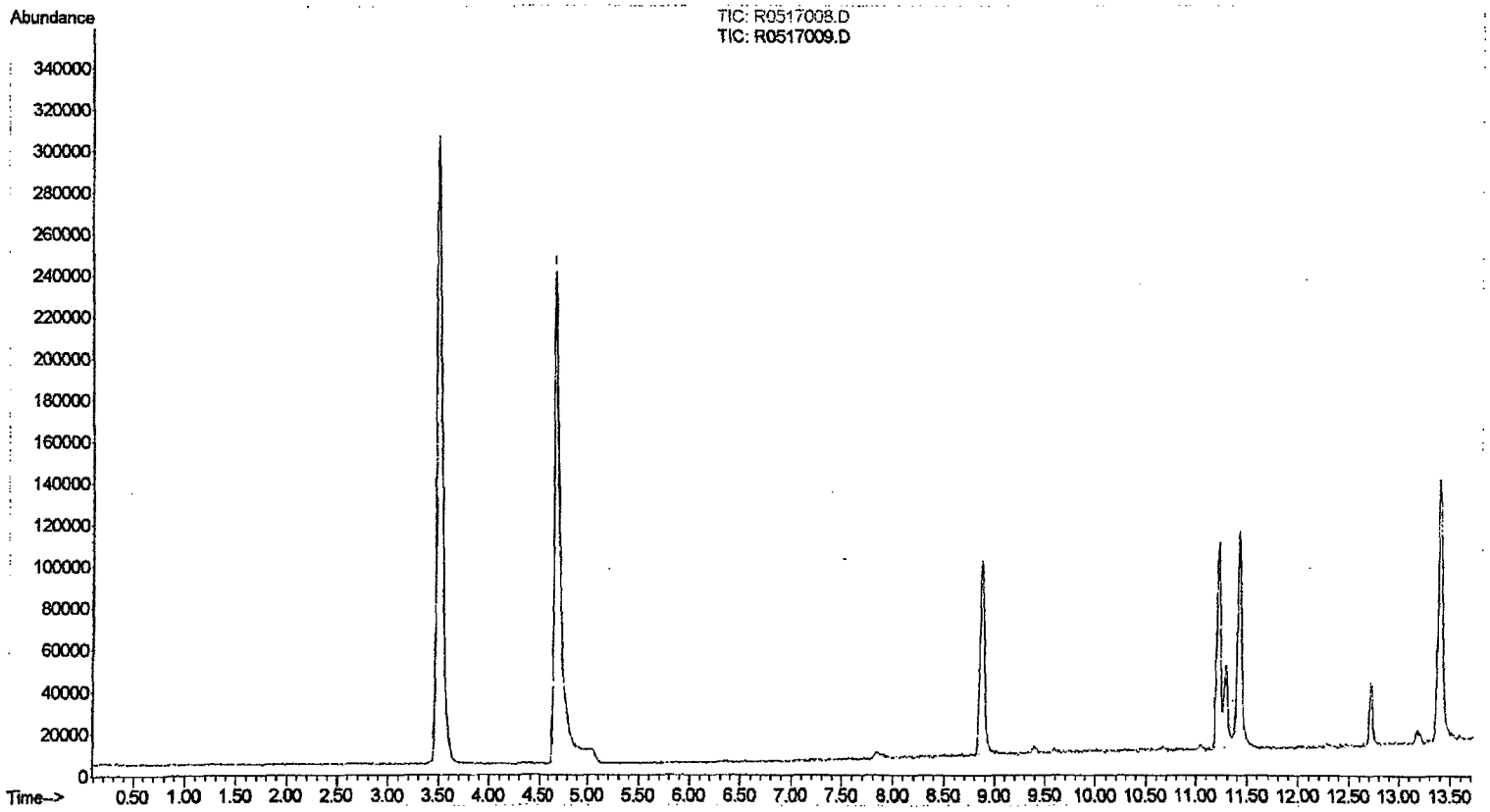
BACK TO MAIN

File : E:\R051700\R0517008.D
Operator : RM
Acquired : 17 May 2000 16:36 using AcqMethod VOA_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-061 matrix blk exp
Misc Info :
Vial Number: 8



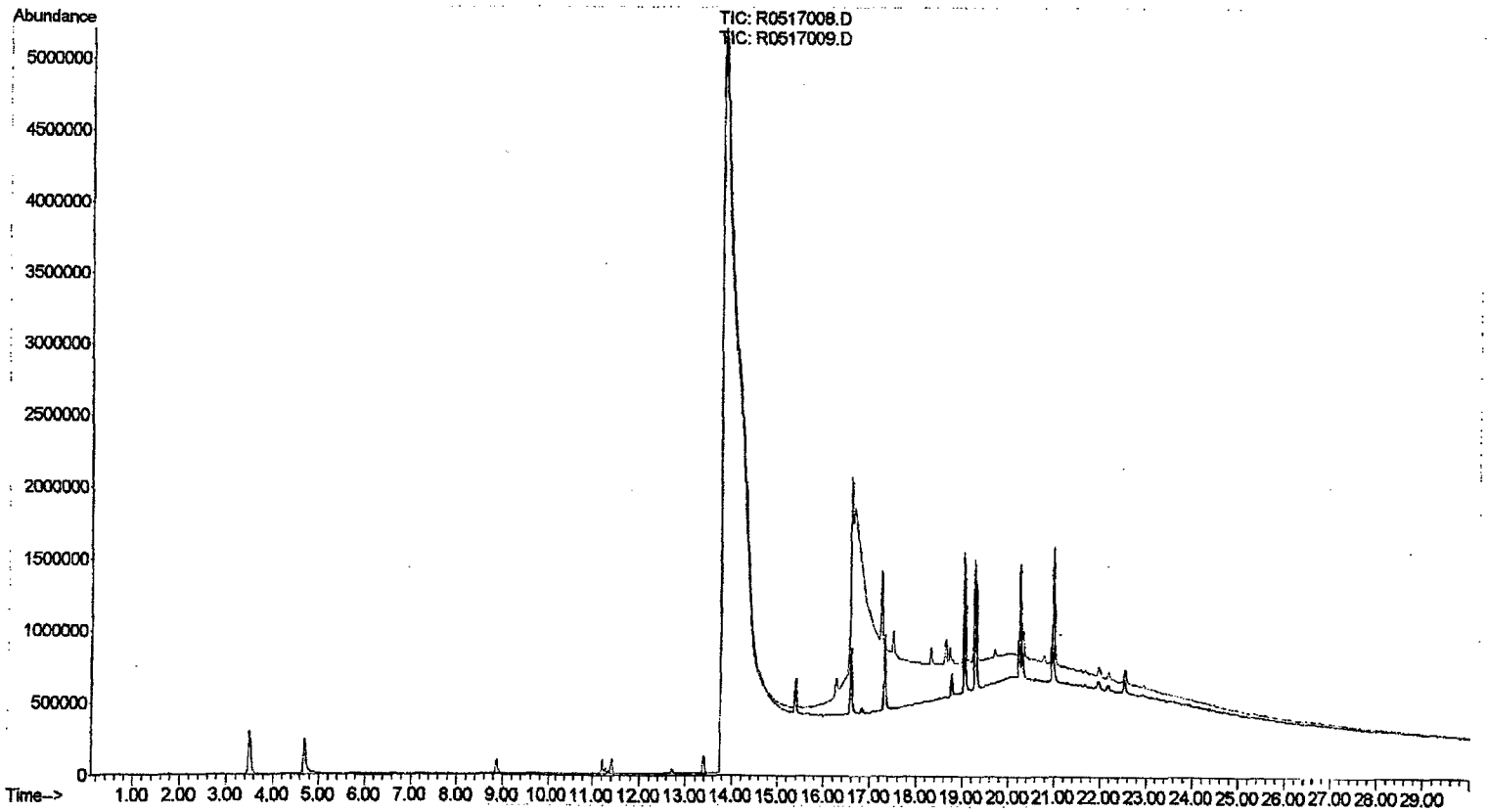
BACK TO MAIN

File : E:\R051700\R0517008.D
Operator : RM
Acquired : 17 May 2000 16:36 using AcqMethod VOA_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-061 matrix blk exp
Misc Info :
Vial Number: 8



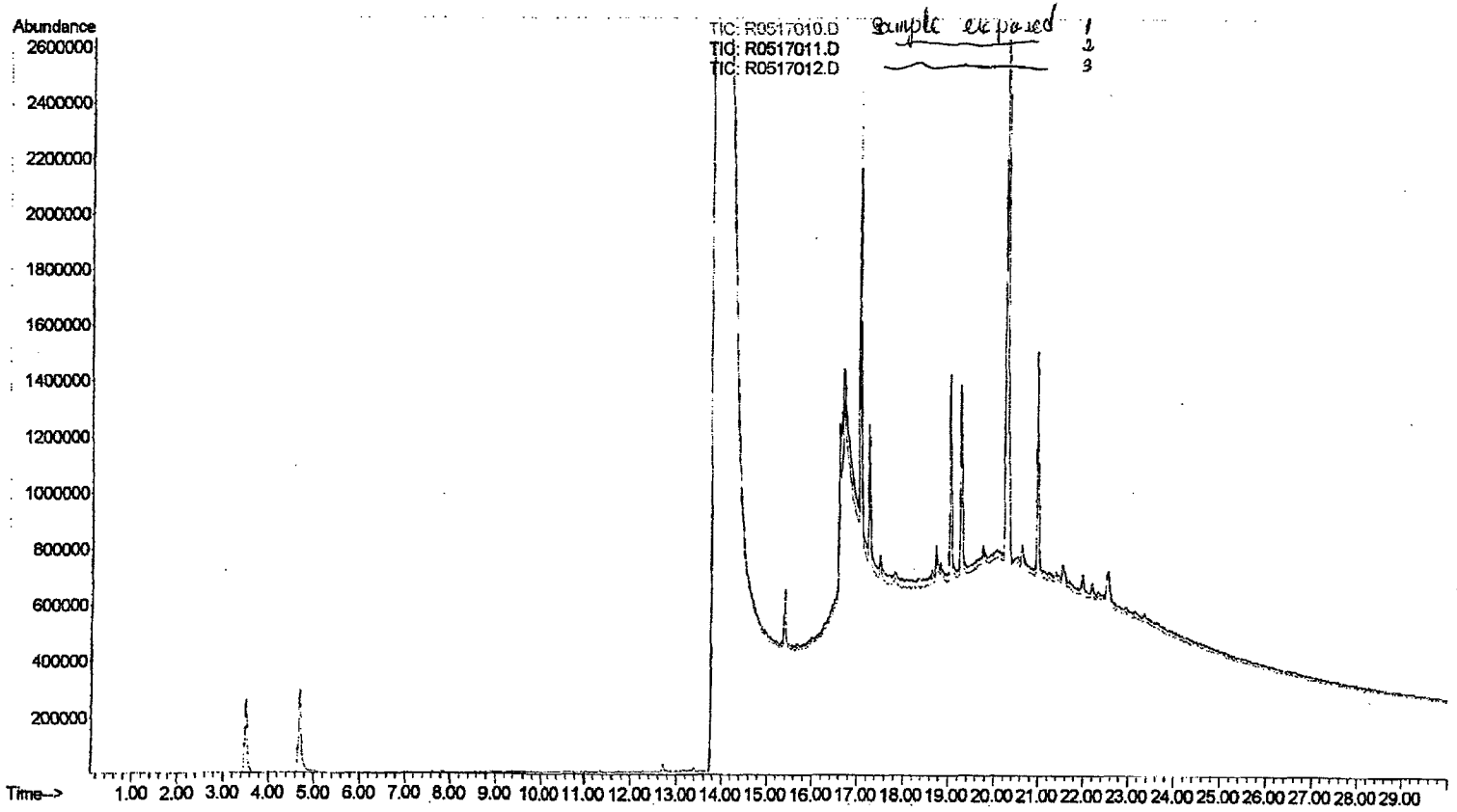
BACK TO MAIN

File : E:\R051700\R0517008.D
Operator : RM
Acquired : 17 May 2000 16:36 using AcqMethod VOA_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-061 matrix blk exp
Misc Info :
Vial Number: 8



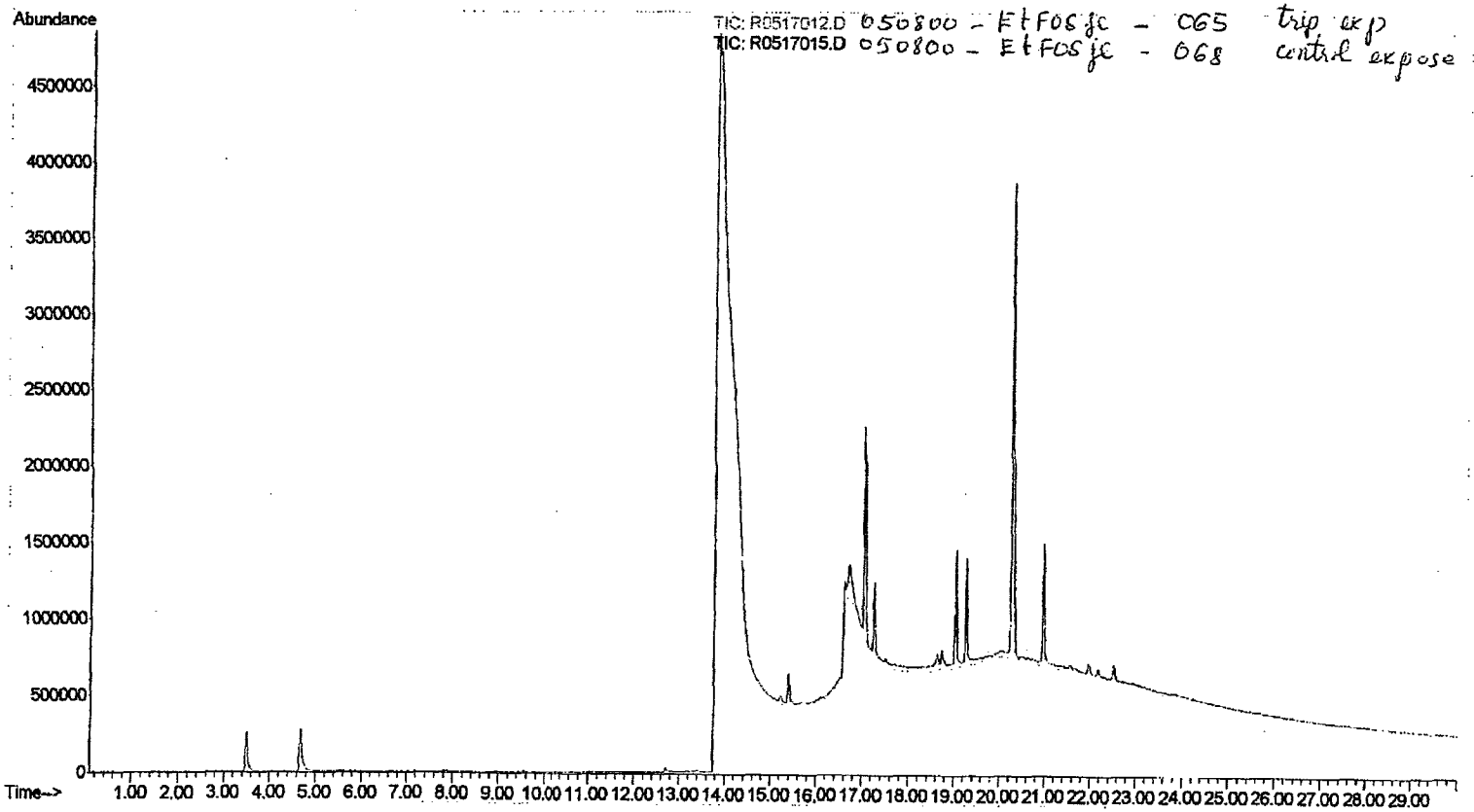
BACK TO MAIN

File : E:\R051700\R0517010.D
Operator : RM
Acquired : 17 May 2000 17:54 using AcqMethod VOA_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-063 sample exp
Misc Info :
Vial Number: 10



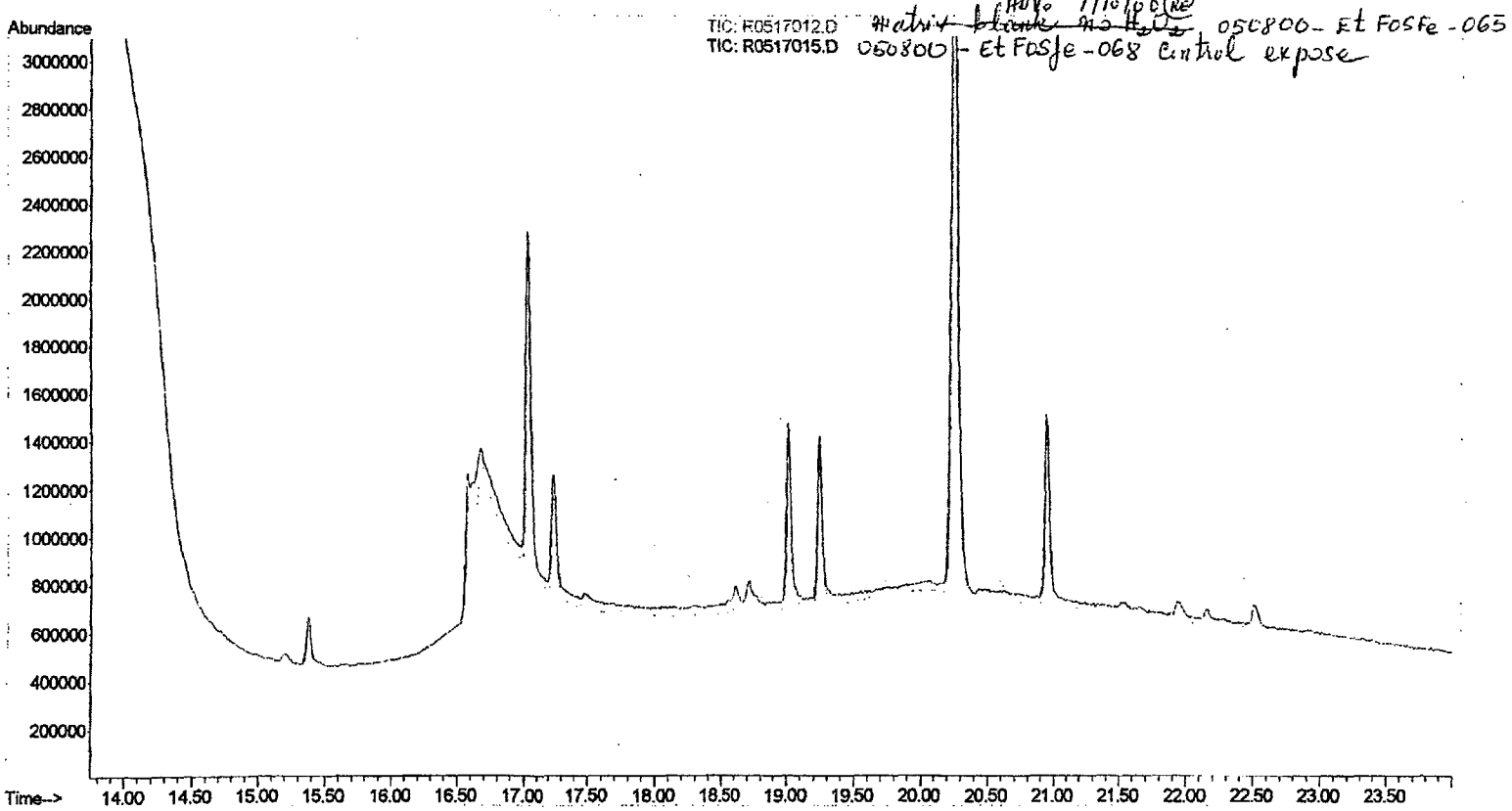
BACK TO MAIN

File : E:\R051700\R0517012.D
Operator : RM
Acquired : 17 May 2000 19:12 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-065 trip exp
Misc Info :
Vial Number: 12



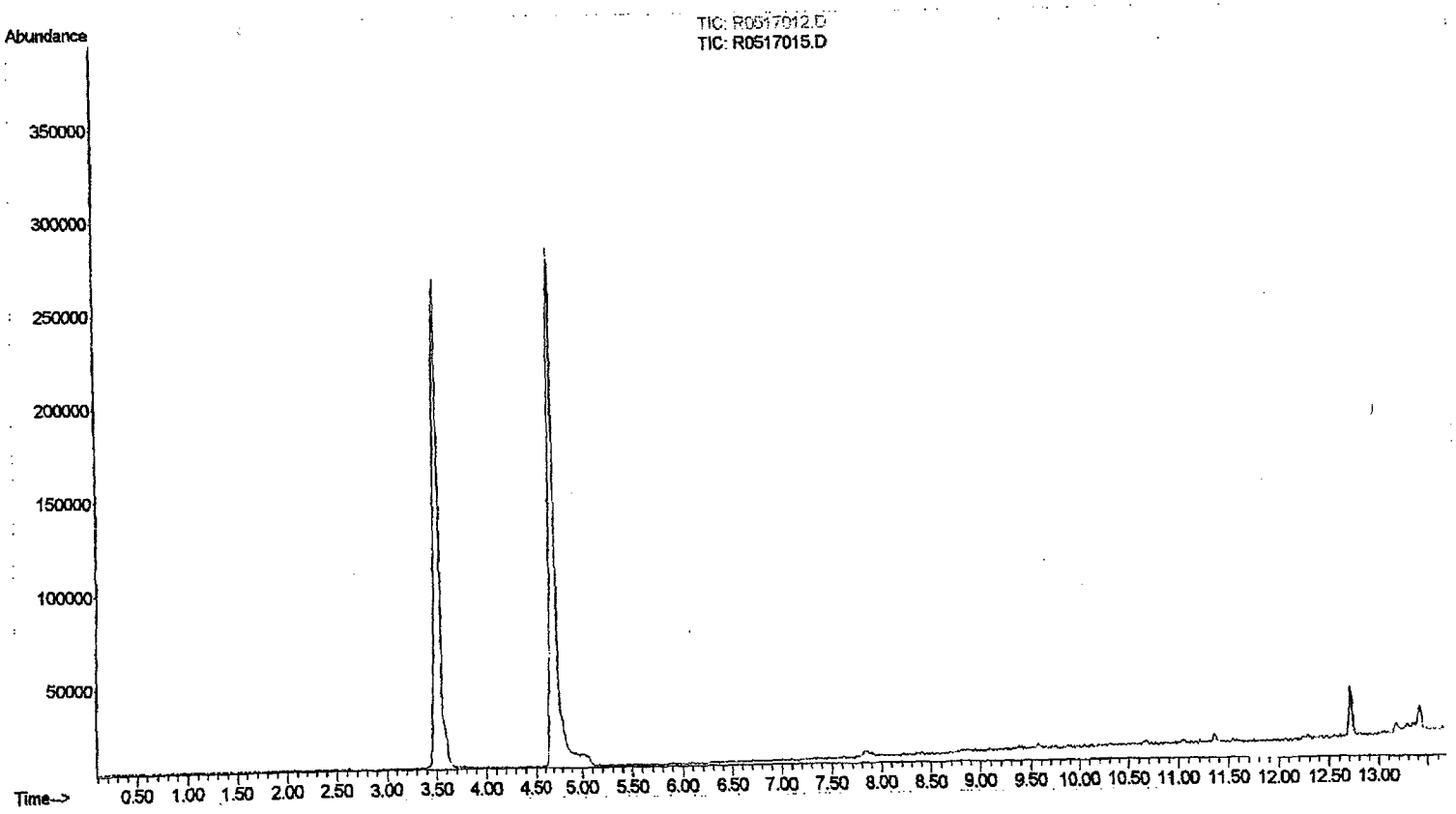
BACK TO MAIN

File : E:\R051700\R0517012.D
Operator : RM
Acquired : 17 May 2000 19:12 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-065 trip exp
Misc Info :
Vial Number: 12



BACK TO MAIN

File : E:\R051700\R0517012.D
Operator : RM
Acquired : 17 May 2000 19:12 using AcqMethod V0A_FC2
Instrument : Rufus
Sample Name: 050800-EtFOSfe-065 trip exp
Misc Info :
Vial Number: 12



BACK TO MAIN

Appendix F: Soil Types and Characterizations

This appendix presents the physical descriptions and chemical characterizations of the three soils used in the present investigation

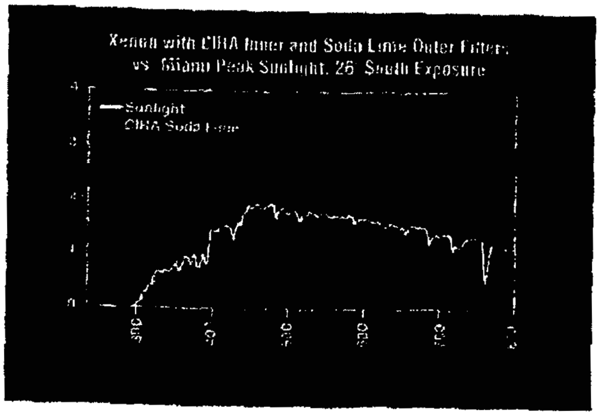
STANDARD LABORATORY SOILS

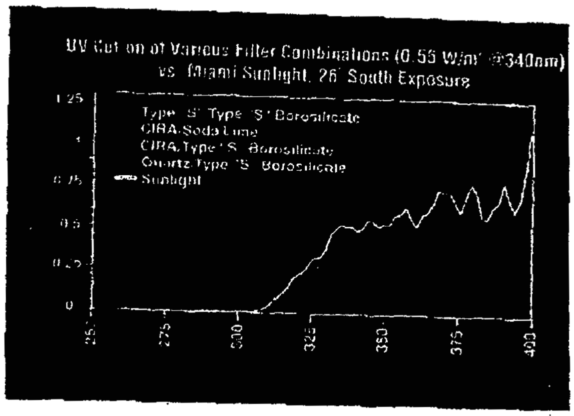
PARAMETER	ST CROIX CO., WI	MORGAN CO., ALA	EPA-SSM
METALS			
Ag, mg/Kg dried basis	<3	<3	<3
Al, mg/Kg dried basis	22000	40000	46000
As, mg/Kg dried basis	<10	<10	<10
Ba, mg/Kg dried basis	210	97	100
Be, mg/Kg dried basis	0.6	<0.5	0.6
Ca, mg/Kg dried basis	3000	1000	86000
Cd, mg/Kg dried basis	<0.5	<0.5	<0.5
Co, mg/Kg dried basis	8	5	6
Cr, mg/Kg dried basis	36	41	25
Cu, mg/Kg dried basis	12	8.5	13
Fe, mg/Kg dried basis	20000	22000	18000
Hg, mg/Kg dried basis	0.04	0.11	0.02
Mg, mg/Kg dried basis	2800	1500	30000
Mn, mg/Kg dried basis	800	120	710
Mo, mg/Kg dried basis	52	84	92
Na, mg/Kg dried basis	120	73	220
Ni, mg/Kg dried basis	18	14	13
P, mg/Kg dried basis	620	150	710
Pb, mg/Kg dried basis	<30	<30	<30
Se, mg/Kg dried basis	<200	<200	<200
Zn, mg/Kg dried basis	49	47	47
EXCHANGE ACTIVITY			
Extractable Ca, meq/100g	8.14	3.50	26.1
Extractable P, meq/100g	0.68	0.10	0.18
Extractable Mg, meq/100g	2.97	0.43	3.58
Extractable Na, meq/100g	0.03	0.02	0.06
Base Saturation %	42	18	100
CEC, meq/100g	28.3	22.0	21.3
ESP, %	0.11	0.09	0.28
SAR, units	0.04	0.05	0.05
NUTRIENTS			
Available P, mg/L	61	5	15
NH3-N, mg/L	2.00	0.25	1.80
NO3-N, mg/L	84	14	6.0
Kjeldahl N, mg/Kg	1470	280	250
ORGANIC MATTER			
TOC, %	1.79	0.277	0.467
OM, %	3.09	0.478	0.805
PHYSIOCHEMICAL			
Field Capacity, %	19.1	22.3	16.0
pHw, units	5.7	4.6	7.7
pHs, units	5.7	4.5	7.5
Lime-req, Tons/Acre	1.8	1.8	NONE
Soluble Salts, mmhos/cm	0.98	0.32	0.66
CLASSIFICATION			
% Clay	22	26	22
% Silt	44	36	26
% Sand	34	38	52
Soil Type	LOAM	CLAY LOAM	SANDY CLAY LOAM
BASE NEUTRAL PESTICIDES	BDL	BDL	BDL
ACID PESTICIDES	BDL	BDL	BDL

BDL = Below Detection Limits

Appendix G: Light Intensity Measurements at 45° South Latitude (Miami FL)

[redacted]





Atlas Xenon Filter Combination

Filter Combinations: Inner Filter Glass	Filter Combinations: Outer Filter Glass	Test Conditions	Wattage	Irradiance Ranges* W/m²: 250-300 nm	300-400 nm	400-800 nm	340 nm	42[illegible] nm
Type "S" Borosilicate	Type "S" Borosilicate	Most common combination for weathering tests.	2500W 7500W	0.1 0.8	28.7 140.8	278.6 1215.4	0.25 1.28	[illegible] [illegible]
Type "S" Borosilicate	Soda Lime	Most common combination for lightfastness tests behind window glass.	2500W 7500W	0.0 0.0	27.8 129.0	280.8 1210.7	0.23 1.40	0.[illegible] 2.7
Quartz	Type "S" Borosilicate	Weathering tests with somewhat more and shorter UV than sunlight.	2500W 7500W	[illegible] 3.1	[illegible] 180.6	[illegible] 1224.1	[illegible] 1.50	[illegible] 2.7
CIRA	Type "S" Borosilicate	Weathering tests requiring full spectrum match and/or cooler test temperatures.	2500W 7500W	0.6 3.2	33.3 168.4	271.6 1228.5	0.31 1.57	0.6 2.9
CIRA	Soda Lime	Weathering tests requiring precise match for solar cut-on, full spectrum match and/or cooler test temperatures.	2500W 7500W	0.0 0.1	31.3 161.3	282.2 1231.8	0.28 1.40	0.6 3.0
Type "S" Borosilicate	Soda Lime	Common combination for testing European automotive interior trim materials. (Requires lantern assembly.)	2500W 7500W	0.0 0.0	23.3 108.6	258.5 1114.7	0.17 0.82	0.5 2.5

Sunlight Measurements

- Made by Atlas - Sun up → Sundo[illegible] TLH - 07/26/00

Average Optimum Natural Daylight	Measured 45° South Cloudless Miami, Florida	0.0	27.8	259.0	0.30	0.6
Peak Natural Daylight	Measured solar noon on the Vernal Equinox at normal incidence Miami, Florida	0.1	66.2	617.0	0.68	1.5
Peak Natural Daylight Standard	Defined for Horizontal Plane (0°) in CIE Publication No. 85 Table 4	0.0	74.8	604.2	0.68	1.5

**Small variations are possible, depending on condition of lamp and filters.*

Appendix H: Characteristics of the Spectral Output of the Suntest Instruments

This appendix contains an Excel spreadsheet of the characteristics of the spectral output of the Suntest Photoreactors used in the present investigation.

Suntest Irradiance in W/m^2*nm

Assuming the use of 300-800nm Global Sensor Only

	Filters Used	Irradiances factored to yield 680 W/m^2 in 300-800nm band
Wavelength nm	IR Q/Suprax (UV)	IR Q/Suprax (UV)
250	0.001	0.001119
252	0	0
254	0	0
256	0	0
258	0.001	0.001119
260	0	0
262	0	0
264	0	0
266	0	0
268	0	0
270	0	0
272	0	0
274	0	0
276	0	0
278	0	0
280	0	0
282	0	0
284	0	0
286	0.003	0.003357
288	0.005	0.005595
290	0.009	0.010071
292	0.014	0.015666
294	0.021	0.023499
296	0.028	0.031332
298	0.045	0.050355
300	0.054	0.060426
302	0.07	0.07833
304	0.085	0.095115
306	0.116	0.129804
308	0.138	0.154422
310	0.151	0.168969
312	0.175	0.195825
314	0.21	0.23499
316	0.24	0.26856
318	0.263	0.294297
320	0.279	0.312201
322	0.329	0.368151

324	0.352	0.393888
326	0.369	0.412911
328	0.4	0.4476
330	0.431	0.482289
332	0.449	0.502431
334	0.475	0.531525
336	0.495	0.553905
338	0.525	0.587475
340	0.549	0.614331
342	0.565	0.632235
344	0.566	0.633354
346	0.587	0.656853
348	0.614	0.687066
350	0.61	0.68259
352	0.635	0.710565
354	0.656	0.734064
356	0.685	0.766515
358	0.662	0.740778
360	0.675	0.755325
362	0.719	0.804561
364	0.714	0.798966
366	0.73	0.81687
368	0.813	0.909747
370	0.858	0.960102
372	0.767	0.858273
374	0.8	0.8952
376	0.827	0.925413
378	0.864	0.966816
380	0.962	1.076478
382	0.992	1.110048
384	0.974	1.089906
386	0.996	1.114524
388	1.028	1.150332
390	1.111	1.243209
392	1.126	1.259994
394	1.227	1.373013
396	1.642	1.837398
398	1.552	1.736688
400	1.243	1.390917
402	1.228	1.374132
404	1.241	1.388679
406	1.284	1.436796
408	1.473	1.648287
410	1.395	1.561005
412	1.551	1.735569
414	1.416	1.584504
416	1.369	1.531911
418	1.426	1.595694
420	1.644	1.839636
422	1.453	1.625907

424	1.472	1.647168
426	1.462	1.635978
428	1.466	1.640454
430	1.466	1.640454
432	1.487	1.663953
434	1.5	1.6785
436	1.566	1.752354
438	1.714	1.917966
440	1.616	1.808304
442	1.616	1.808304
444	1.57	1.75683
446	1.563	1.748997
448	1.573	1.760187
450	2.267	2.536773
452	2.031	2.272689
454	1.796	2.009724
456	1.811	2.026509
458	2.127	2.380113
460	1.835	2.053365
462	3.267	3.655773
464	2.476	2.770644
466	2.541	2.843379
468	5.277	5.904963
470	2.487	2.782953
472	1.922	2.150718
474	2.924	3.271956
476	1.837	2.055603
478	1.813	2.028747
480	2.289	2.561391
482	2.516	2.815404
484	2.651	2.966469
486	1.952	2.184288
488	1.842	2.061198
490	1.898	2.123862
492	3.012	3.370428
494	2.089	2.337591
496	1.871	2.093649
498	1.888	2.112672
500	1.898	2.123862
502	1.973	2.207787
504	2.005	2.243595
506	1.94	2.17086
508	1.927	2.156313
510	1.934	2.164146
512	1.963	2.196597
514	2.013	2.252547
516	2.031	2.272689
518	2.021	2.261499
520	1.995	2.232405
522	1.971	2.205549

524	1.98	2.21562
526	1.966	2.199954
528	1.978	2.213382
530	1.954	2.186526
532	1.932	2.161908
534	1.942	2.173098
536	2.008	2.246952
538	2.014	2.253666
540	2.113	2.364447
542	1.996	2.233524
544	1.977	2.212263
546	1.962	2.195478
548	1.921	2.149599
550	1.876	2.099244
552	1.84	2.05896
554	1.938	2.168622
556	2.17	2.42823
558	2.106	2.356614
560	1.936	2.166384
562	1.912	2.139528
564	1.749	1.957131
566	1.706	1.909014
568	1.77	1.98063
570	1.997	2.234643
572	2.032	2.273808
574	1.802	2.016438
576	1.624	1.817256
578	1.572	1.759068
580	1.654	1.850826
582	2.215	2.478585
584	2.034	2.276046
586	1.738	1.944822
588	2.118	2.370042
590	2.159	2.415921
592	1.996	2.233524
594	2.185	2.445015
596	1.607	1.798233
598	1.492	1.669548
600	1.471	1.646049
602	1.37	1.53303
604	1.263	1.413297
606	1.207	1.350633
608	1.184	1.324896
610	1.292	1.445748
612	1.494	1.671786
614	1.31	1.46589
616	1.631	1.825089
618	2.672	2.989968
620	2.172	2.430468
622	1.416	1.584504

624	1.181	1.321539
626	1.256	1.405464
628	1.251	1.399869
630	1.51	1.68969
632	2.325	2.601675
634	1.246	1.394274
636	0.959	1.073121
638	0.927	1.037313
640	0.834	0.933246
642	0.856	0.957864
644	0.876	0.980244
646	1.013	1.133547
648	1.571	1.757949
650	1.431	1.601289
652	1.12	1.25328
654	1.071	1.198449
656	0.86	0.96234
658	0.801	0.896319
660	1.103	1.234257
662	0.763	0.853797
664	0.762	0.852678
666	0.855	0.956745
668	1.037	1.160403
670	0.575	0.643425
672	0.682	0.763158
674	0.912	1.020528
676	0.526	0.588594
678	0.567	0.634473
680	0.514	0.575166
682	0.738	0.825822
684	1.065	1.191735
686	1.214	1.358466
688	2.331	2.608389
690	1.16	1.29804
692	0.73	0.81687
694	0.603	0.674757
696	0.432	0.483408
698	0.688	0.769872
700	0.347	0.388293
702	0.327	0.365913
704	0.298	0.333462
706	0.31	0.34689
708	0.275	0.307725
710	0.424	0.474456
712	2.069	2.315211
714	0.594	0.664686
716	0.302	0.337938
718	0.289	0.323391
720	0.254	0.284226
722	0.297	0.332343

724	0.384	0.429696
726	0.592	0.662448
728	0.817	0.914223
730	0.593	0.663567
732	0.634	0.709446
734	0.472	0.528168
736	0.316	0.353604
738	0.375	0.419625
740	1.097	1.227543
742	0.368	0.411792
744	0.272	0.304368
746	0.264	0.295416
748	0.439	0.491241
750	0.356	0.398364
752	0.231	0.258489
754	0.273	0.305487
756	0.406	0.454314
758	0.823	0.920937
760	1.344	1.503936
762	0.554	0.619926
764	1.555	1.740045
766	1.114	1.246566
768	0.388	0.434172
770	0.194	0.217086
772	0.152	0.170088
774	0.188	0.210372
776	0.21	0.23499
778	0.247	0.276393
780	0.388	0.434172
782	0.327	0.365913
784	0.225	0.251775
786	0.171	0.191349
788	0.335	0.374865
790	0.693	0.775467
792	0.137	0.153303
794	0.18	0.20142
796	0.326	0.364794
798	0.632	0.707208
800	0.233	0.260727

Total Integrated Irradiance in 300-800nm Wavelength Band		
	607.6 W/m^2	680.0 W/m^2