

AR 226-0056

EFT-2

PHOTODEGRADATION

TEST SUBSTANCE

Identity: Perfluorooctanesulfonate; may also be referred to as PFOS or FC-95. (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluoro-, potassium salt, CAS # 2795-39-3)

Remarks: Testing is in progress.

000211

PHOTODEGRADATION

TEST SUBSTANCE

Identity: Perfluorooctanesulfonate; may also be referred to as PFOS or FC-95. (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluoro-, potassium salt, CAS # 2795-39-3)

Remarks field: The test substance is a white powder. The test substance used was ^{14}C labeled (285 dpm/ μg). Purity of the test substance is not described. This testing is currently being repeated using current procedures and best available practices.

METHOD

Method/guideline followed: Procedure as described in the Federal Register (Volume 43, No. 132-Monday, July 10, 1978) by the U.S. Environmental Protection Agency.

Type (test type): Simulated sunlight

GLP (Y/N): No

Year: 1978

Light Source: General Electric F-40BL fluorescent black light

Light Spectrum (nm): Max output at ~360 nm and essentially no output below 300 nm. Spectral energy characterized from 290-600 nm.

Intensity:

Wavelength	Watts Radiated
290 – 300	0.090
310 – 320	0.235
320 – 340	1.410
340 – 360	1.910
360 – 380	2.310
380 – 400	1.680
400 – 500	2.300
500 – 600	0.340

Spectrum of substance (max lambda, max epsilon and epsilon 295):
Not determined.

Remarks field:

- **Test medium (air, water, soil, other - specify):** Distilled water
- **Duration:** 30 days
- **Positive Controls:** None
- **Negative Controls:** None

000212

Photolyzate samples were collected after irradiation intervals of 0, 3, 7, 15, and 30 days. Samples were analyzed using a Liquid Scintillation Counter (LSC), TLC-Autoradiograph and Gas Chromatography.

RESULTS

Concentration of Substance: 50 mg/L

Temperature °C: 23±3°C

Degradation %: 0% after 30 days

Remarks field: No photodegradation of the test substance was detected in this study. Essentially the same analysis results were obtained for the 30-day photolyzate sample (no photoproducts formed) as the 0-day sample.

Radiocarbon assays at 0 and 30 days also indicate no significant amount of product was volatilized during the study.

CONCLUSIONS

No photodegradation products were detected in this study using simulated sunlight, indicating the test substance does not undergo photolysis.

Submitter: 3M Company, Environmental Laboratory, P.O. Box 33331, St. Paul, Minnesota, 55133

DATA QUALITY

Reliability: Klimisch ranking 2. Photolysis study is being repeated using currently available procedures and best practices using a sample with characterized purity.

REFERENCES

3M Technical Report "FC-95/PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT." J. W. Todd, Project 9776750202, January 9, 1979

OTHER

Last changed: 5/2/00

SUMMARY OF PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT ON THE POTASSIUM SALT OF PERFLUOROOCTANESULFONIC ACID

Exposure Conditions

This study was performed on the potassium salt of perfluorooctanesulfonic acid as described in Federal Register (Volume 43, No. 132-Monday, July 10, 1978) by the U.S. Environmental Protection Agency. The test solution contained 50 ppm of ^{14}C labeled potassium perfluorooctanesulfonate (285 dpm/ug) in 2 liters of D.I. water. The specific activity of the solution was 14,250 dpm/ml (0.0064 $\mu\text{C}/\text{ml}$).

The photoreactor contained a General Electric F-40BL fluorescent black light with a maximum output at about 360 nm and essentially no output below 300 nm. The temperature of the reactor was controlled at $23 \pm 3^\circ\text{C}$ by circulating tap water. Photolyzate samples were collected after irradiation intervals of 0, 3, 7, 15, and 30 days. Collected samples were removed through the reactor drain port and were refrigerated until analyzed.

Analysis of Photoproducts by TLC-Autoradiography

A 100 ml aliquot of the 0 and 30 day photolyzate samples were concentrated with a rotary vacuum evaporator and a water bath to dryness, redissolved in 3 ml of methanol, and transferred with two 3 ml washings into Kuderna-Danish concentrator tubes. Each solution were further concentrated to 1 ml.

A 10 μl aliquot of each sample (equivalent to 1 ml of the original photolyzate solution) was transferred onto a Thin Layer Chromatography (TLC) plate using a 10 μl syringe. Each plate was developed two-dimensionally with ethyl acetate/acetic acid (95/5) followed by ethyl acetate/chloroform/formic acid/water (65/20/10/5). After air drying, the spots were scraped and quantified for radioactive carbon.

Analysis of Photoproducts by Gas Chromatography

Photolyzate samples from days 0 and 30 were analyzed by acidifying 2.0 ml of each in a 4-dram vial with 0.2 ml of concentrated HCl and extracting with two 2 ml portions of diethyl ether. The combined extracts of each sample were concentrated to 0.1 ml in a 10-ml Kuderna-Danish concentrator tube using a nitrogen purge. The concentrated samples were methylated with 0.4 ml of diazomethane methylating solution and mixed well.

Using a 10 μl syringe, 6 μl of sample (equivalent to 1.5 μg of the compound of interest) was injected, via on-column injection at 150°C , into a Model 7620 Hewlett-Packard gas chromatograph with a 6 ft X 1/8 in. O.D. stainless steel packed column with 5% OV-17 silicone on Chromosorb G support. The GC column oven was temperature programmed from 60 to 150°C at $15^\circ\text{C}/\text{min}$. Analytes were detected with a microwave sustained helium plasma detector from Applied Chromatography Systems Limited, Luton, England. The detector was operated in the fluorine and sulfur modes simultaneously with outputs to a dual-pen recorder.

Results

No photodegradation products were detected in this study. Similar radiocarbon assays (with good analyte recoveries) and similar gas chromatograms were obtained from the 0 and 30 day samples.

TECHNICAL REPORT SUMMARY

Date 1-9-79

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

Important - If report is printed on both sides of paper, send two copies to TCC.)

Division	Commercial Chemicals Division - Agrichemicals Project		Dept. Number	3068
Project	Service to TOSCA		Project Number	9776750202
Report Title	FC-95/PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT		Report Number	001
To	R. A. Prokop			
Author(s)	J. W. Todd		Employee Number(s)	43953
Notebook Reference	Agrichemical Request 888		No. of Pages Including Coversheet	13
SECURITY	☐ Open (Company Confidential)	☐ Closed (Special Authorization)	3M CHEMICAL REGISTRY	New Chemicals Reported ☐ Yes ☒ No

KEYWORDS:
(Select terms from 3M
Thesaurus. Suggest other
applicable terms.)

to/Radiography
composition
vironment
s-Chromatography
yer/Chromato-
graphy
otolysis
diotracer
intillation

CURRENT OBJECTIVE:

Investigate the photolytic stability of FC-95 as a function of irradiation time and identify any major photo products.

REPORT ABSTRACT: (200-250 words) This abstract information is distributed by the Technical Communications Center to alert 3M'ers to Company R&D.

Irradiation of a 50 ppm aqueous solution of FC-95 for 30 days resulted in no detected photoproducts on analysis by thin-layer-chromotography/radioautography, and by gas chromatography of derivatized samples using a microwave plasma detector. The irradiation source produced 300 nm and longer wavelength light to simulate natural sunlight.

FC-95/PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT

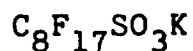
INTRODUCTION

It is generally acknowledged that manufactured chemicals may find their way into the environment in various degrees and by various means. Once in the environment they may be destroyed or chemically altered by the action of sunlight (Crosby and Li, 1969). This study investigated the possible photodegradation of FC-95 in distilled water on exposure to simulated sunlight (Kohler, 1965). This study was conducted essentially as recommended by the Environmental Protection Agency (Federal Register).

EXPERIMENTAL

1. Sample Materials

FC-95 is the potassium salt of perfluorooctanesulfonic acid.



The major component is the straight-chain C_8 but some branched chain isomers and other homologs also are present.

FC-95 Water Solution.

A 50 ppm solution of FC-95- ^{14}C (285 dpm/ μg) was prepared by dissolving 100.0 mg of FC-95 in 2 liters of distilled water. The resulting solution had a specific activity of 14,250 dpm/ml (0.0064 $\mu\text{C}/\text{ml}$).

2. Analysis Instruments/Materials

Liquid Scintillation Counter (LSC)

Nuclear-Chicago Mark I

Rotary Evaporator

Büchi Rotovapor R

Kuderna-Danish Concentrator

10 ml concentrator tube - Kontes No. K-570050
Reflux column - Kontes No. K-569251
Heated water bath

000216

Thin-Layer Chromatography (TLC) plates

MERCK Silica Gel 60 F-254, 0.25 mm thickness and 20 x 20 cm size
 1st developing solvent - ethyl acetate/acetic acid 95/5
 2nd developing solvent - ethyl acetate/chloroform/formic acid/water, 65/20/10/5

X-Ray Film

KODAK NS-5T, 8 x 10 inch size

Gas Chromatography System (GC)

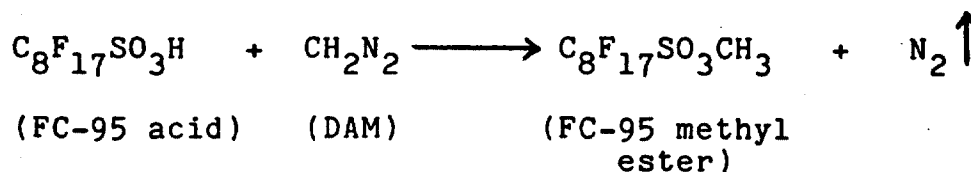
Gas chromatograph - Hewlett-Packard Model 7620
 Column - 6 ft 1/8 in od stainless steel packed with 5% OV-17 silicone on CHROMOSORB G support.
 Column temperature - 60 to 150 programmed at 15°C/min.
 Injector - on-column at 150°C
 Detector - microwave sustained helium plasma from Applied Chromatography Systems Limited, Luton, England

DIAZALD

DIAZALD is Aldrich Chemical Company's trade name for N-methyl-N-nitroso-p-toluenesulfonamide. It is used to prepare diazomethane, an analytical reactant chemical.

Diazomethane solution - Alcohol Free.

Diazomethane (DAM) was used to convert acidified FC-95 into its corresponding methyl sulfonate ester just prior to gas chromatographic analysis.



The DAM reagent used must be free of alcohols or the desired reaction product will not form or will degrade after it has formed. The alcohol-free DAM was prepared essentially as recommended by Aldrich:

A solvent mixture consisting of 35 ml of 2-(2-ethoxyethoxy)-ethanol and 20 ml of diethyl ether was added to a solution of 6 grams of potassium hydroxide dissolved in 10 ml of water. This mixture was

placed in a 100 ml long-necked distilling flask fitted with a dropping funnel, an efficient condenser and a water bath at 70°C. As the distillation of the ether started a solution of 21.5 g of DIAZALD in about 200 ml of ether was added through the dropping funnel over about 20 minutes. The ethereal DAM solution was collected in a 250-ml Erlenmeyer flask cooled in an ice bath. The flask contents were transferred into a bottle, sealed with a TEFLON-lined cap and stored in a freezer.

3. Irradiation

The preparative photoreactor used (Crosby and Tang, 1969) is illustrated in Figure 1. The lamp employed was a General Electric F-40BL fluorescent black light with maximum output at about 360 nm and essentially no output below 300 nm (Table I, General Electric Co.). The temperature was controlled at $23 \pm 3^\circ\text{C}$ by circulating tap water through flexible plastic tubing wrapped around the reaction chamber. Nitrogen was passed through the photolysis solution at 20 ml/min to provide mixing. The exit port was connected to a vapor trap. The trap consisted of a 6 x 3/4 in. glass tube containing first XAD-2 resin and then charcoal. The photolyzate was sampled after irradiation intervals of 0, 3, 7, 15 and 30 days. The samples were removed through the reactor drain port and were refrigerated until analyzed.

4. Radiocarbon Recovery

The photolyzate samples were assayed for radiocarbon by LSC to determine radiocarbon recovery as a function of irradiation time. Similar results were obtained for all samples. Results for the 30 and 0-day samples are presented in Tables II and III, respectively.

5. Investigation for Photoproducts by TLC-Autoradiography

Aliquots of the 30 and 0-day photolyzates were reduced in volume 100-fold before TLC analysis. First a 100-ml aliquot of each sample was concentrated to about 5 ml using a rotary vacuum evaporator with a 40-50 C water bath, 50 ml of acetonitrile was added and the rotovac'ing continued to just dryness (Acetonitrile was added to expeditiously remove remaining water as an azeotrope and thereby minimize possible loss of radiocarbon).

000218

The sample solids were dissolved in 3 ml of methanol and quantitatively

transferred into a Kuderna-Danish concentrator tube with two additional 3-ml washings. Reflux tubes were attached and the concentrator tubes were immersed in a 65-74°C water bath. The tube contents were concentrated to exactly 1 ml.

A 10.0 μ l aliquot of each sample concentrate (equivalent to 1.0 ml of the original photolyzate solution) was transferred onto a TLC plate using a 10 μ l microsyringe. Each plate was developed two-dimensionally, first with ethyl acetate/acetic acid (95/5) and then with ethyl acetate/chloroform/formic acid and water (65/20/10/5). The air-dried TLC plates were then radioautographed. Figures 2 and 3 are pictures of the 30 and 0-day radioautographs, respectively.

Various component spots and areas on each TLC plate were quantitated for radiocarbon by carefully scraping the silica gel from the plate and LSC counting. The results are presented in Tables II and III.

6. Investigation for Photoproducts by Gas Chromatography

Sulfonate salts as FC-95 are not analyzable by gas chromatography. Recent work has shown that FC-95 is analyzable if acidified, isolated from the water matrix and methylated with DAM. The 30 and 0-day photolyzate samples were analyzed by this method (3M Central Research Laboratory). The procedure used is summarized below:

Two ml of the photolyzates were pipetted into 4-dram vials. Each sample was acidified with 0.2 ml of concentrated hydrochloric acid and the resulting acids were quantitatively extracted with two 2 ml portions of diethyl ether. The combined ether extracts were concentrated to 0.1 ml in a 10-ml Kuderna-Danish concentrator tube using a nitrogen purge.

The concentrated extracts were diluted to 0.4 ml with DAM solution and mixed well. Using a 10 μ l microsyringe, 6 μ l sample portions (equivalent to 1.5 μ g of FC-95) were injected into the gas chromatograph for analysis. The microwave plasma detector was operated simultaneously in the fluorine and sulfur modes with outputs to a dual-pen recorder. The chromatograms for the 0 and 30-day photolyzate samples are presented in Figure 4.

This analysis method is unique in that 1) there are only a few microwave plasma detectors in this country and 2) methyl esters of sulfonic and fluorosulfonic acids generally have been considered to be too unstable for gas chromatographic analysis. The analysis results here demonstrate that FC-95 indeed can be analyzed by gas chromatography.

Several less obvious parameters also are important: The DAM solution should be freshly prepared, preferably the same day it is used. Excess DAM is necessary in the analyzed sample solution and its presence is evidenced by a characteristic yellow color. Several injections of sample may be necessary to passivate the column before accurate and repeatable results are obtained. Presence of diazomethane in the analyzed sample produces interfering peaks when the more conventional flame ionization and electron capture detectors are used but does not interfere with the microwave plasma detector used here.

RESULTS

No photodegradation of FC-95 was detected in this study. Essentially the same analysis results were obtained for the 30-day photolyzate sample (no photoproducts formed) as the 0-day sample.

Similar radiocarbon assays were obtained. (Tables II and III). Therefore no significant amount of radiocarbon was volatilized during the photolysis and so the contents of the vapor trap were not analyzed.

Similar TLC-radioautographs were obtained indicating no change in composition in the 30-day sample compared to the 0-day sample (Figure 2 and 3). Quantitative measurement of radiocarbon in various TLC spots and background areas show similar radiocarbon distribution and good recoveries (Tables II and III).

Similar gas chromatograms were obtained further confirming the same composition of the 30 and 0-day samples (Figure 4).

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REFERENCES

Crosby, D.G. and Li, M. 1969. Herbicide Photodecomposition, Chapter 12:321-363 in Degradation of Herbicides, Kearney, P.C. and Kaufman, D.D. (ed), Marcel Dekker Inc. New York, 394 p.

General Electric Company, Information from their Lamp Division, F40BL black light bulb.

Koller, L.R. 1965. Ultraviolet Radiation, 2nd Ed. Wiley, New York. 312 p.

Federal Register, Volume 43. No. 132-Monday, July 10, 1978.

Crosby, D.G. and Tang, C.S., J. Agric. Food Chem., 17, 1041 (1969).

3M Central Research Laboratory, Analytical Request A-70732.

Figure 1 - Photoreactor

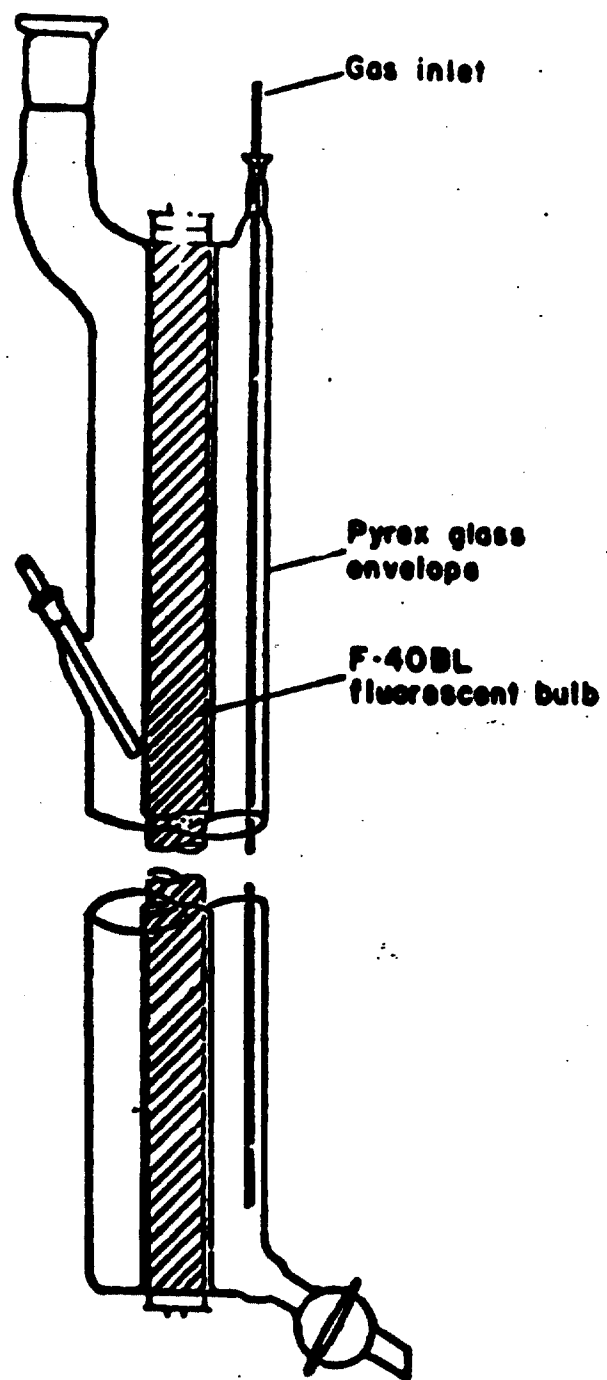


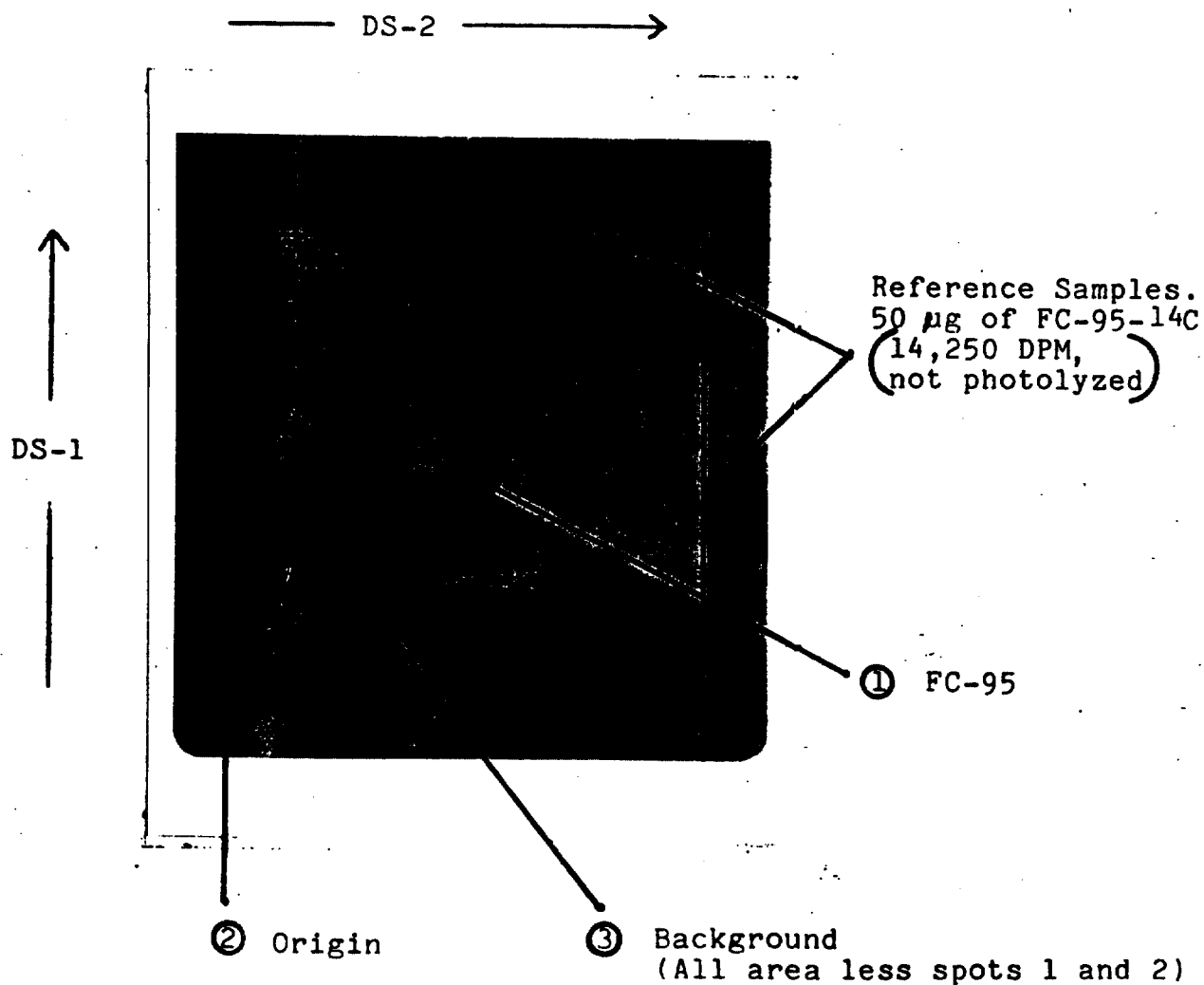
Table I - Spectral Energy Distribution for a GE F40BL Black Light Bulb

<u>Wavelength</u>	<u>Watts Radiated</u>
290 - 300	0.090
310 - 320	0.235
320 - 340	1.410
340 - 360	1.910
360 - 380	2.310
380 - 400	1.680
400 - 500	2.300
500 - 600	0.340

Maximum intensity
at about 360 nm

Figure 2 - Photograph of TLC Radioautograph,
30-Day FC-95 Photolyzate

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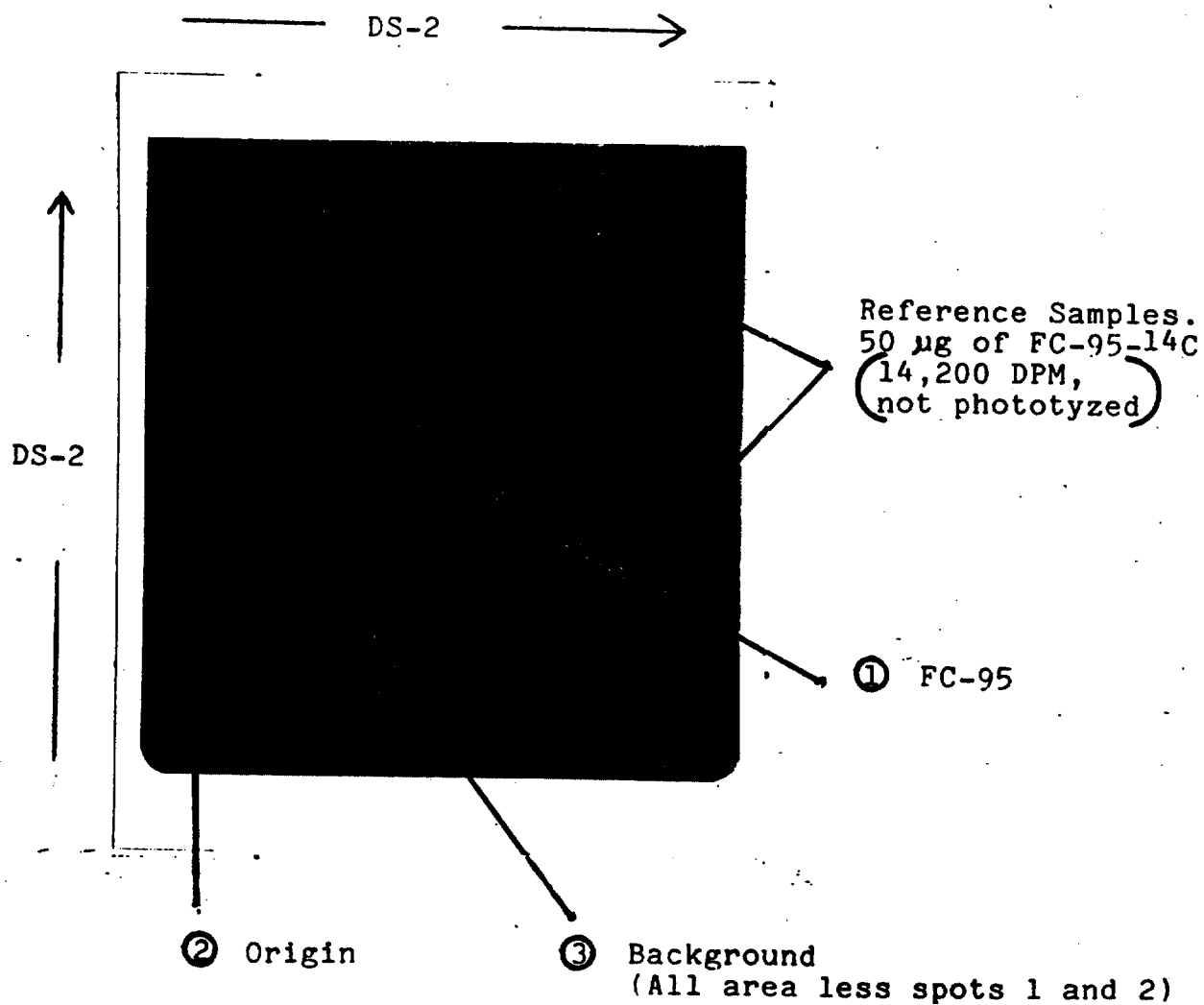
DS-1 = Developing Solvent #1, ethyl acetate/acetic acid, 95/5.

DS-2 = Developing Solvent #2, ethyl acetate/chloroform/formic acid/water, 65/20/10/5.

000224

Figure 3 - Photograph of TLC Radioautograph,
0-Day FC-95 Photolyzate

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DS-1 = Developing Solvent #1, ethyl acetate/acetic acid, 95/5.

DS-2 = Developing Solvent #2, ethyl acetate/chloroform/formic acid/water, 65/20/10/5.

000225

Table II - Radiocarbon recovered in 30-Day Photolyzate Solution and TLC Plate Scrapings (FIGURE 2)

<u>Sample Solution</u>		<u>TLC Plate Scrapings</u>			
<u>DPM/ml</u>	<u>Relative %</u>	<u>Area</u>	<u>Description</u>	<u>DPM(per ml)*</u>	<u>% Recovery</u>
14,430	[100]	1	FC-95	13,873	96
		2	Origin.	49	0.3
		3	"Background"	1,276	9
		Total		15,198	103

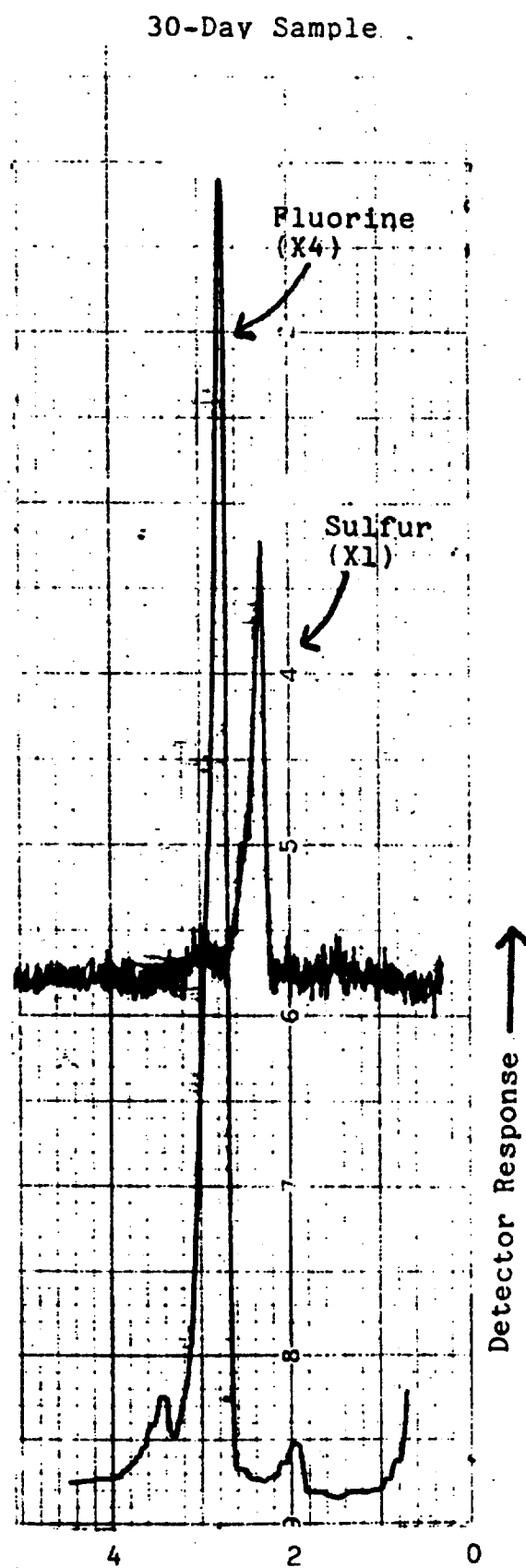
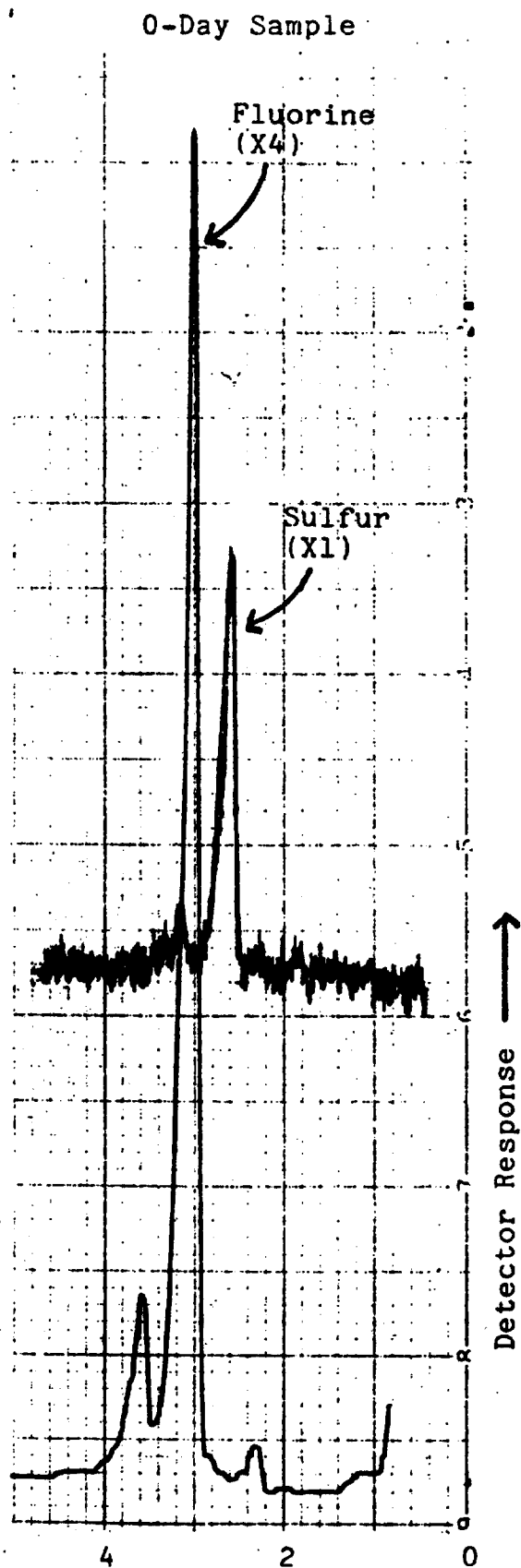
* The amount of ^{14}C radioactivity on the plate is equivalent to 1 ml of the original photolyzate solution.

Table III - Radiocarbon recovered in 0-Day Photolyzate Solution and TLC Plate Scrapings (FIGURE 3)

<u>Sample Solution</u>		<u>TLC Plate Scrapings</u>			
<u>DPM/ml</u>	<u>Relative %</u>	<u>Area</u>	<u>Description</u>	<u>DPM(per ml)*</u>	<u>% Recovery</u>
14,425	[100]	1	FC-95	13,465	93
		2	Origin.	26	0.2
		3	"Background"	1,600	11
		Total		15,091	104

* The amount of ^{14}C radioactivity on the plate is equivalent to 1 ml of the original photolyzate solution.

Figure 4 - Microwave Plasma Gas Chromatogram of Derivatized Photolyzate Samples.



000227