PHOTODEGRADATION

TEST SUBSTANCE

Identity: Perfluorooctanoic acid, ammonium salt; may also be referred to as PFOA ammonium salt, Ammonium perfluorooctanoate, PFO, FC-116, FC-126, FC-169, or FC-143. (Octanoic acid, pentadecafluoro ammonium salt, CAS # 3825-26-1)

Remarks: The test substance used was ^{14}C labeled (358 dpm/μg). It's purity was not sufficiently characterized, though current information indicates it is a mixture of 96.5 - 100% test substance and 0 – 3.5% C_6, C_7, and C_9 perfluoro analogue compounds. 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 completed:1979
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.

The test solution was created by dissolving 140.0 mg of the test substance in 2.8 liters of distilled water. The resulting solution had a specific activity of 17,320 dpm/mL (0.0078 μC/mL).

Remarks:

- **Test medium:** Distilled water
- **Duration:** 30 days
- **Positive Controls:** None
- **Negative Controls:** None

Photolyzate samples were collected after irradiation intervals of 0, 1, 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: 22±2°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. Testing meets the criteria for quality testing at the time it was conducted. However, sample purity was not properly characterized.

REFERENCES

3M Technical Report "FC-143 PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT." J. W. Todd, Project 9776750202, Report number 002, February 2, 1979

OTHER

Last changed: 5/24/00

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TECHNICAL REPORT SUMMARY

Date: 2-2-79

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 - Agrichemical Project	Dept. Number: 3068
Project: Service to TOSCA	Project Number: 9776750202
Report Title: FC-143 PHOTOLYSIS STUDY USING SIMULATED SUNLIGHT	Report Number: 002
To: R. A. PROKOP	
Author(s): J. W. TODD	Employee Number(s): 43953
Notebook Reference: Agrichemical Request 994	No. of Pages Including Coversheet: 13

SECURITY ▶ ☐ Open ☒ Closed (Special Authorization) | 3M CHEMICAL REGISTRY ▶ New Chemicals Reported ☐ Yes ☒ No

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

uto/Radiography
ecomposition
nvironment
as-Chromatography
ayer/Chromato-
graphy
hotolysis
adiotracer
cintillation

CURRENT OBJECTIVE:

Investigate the photolyic stability of FC-143 as a function of irradiation time and identify any major photoproducts.

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-143 for 30 days resulted in no detected photoproducts on analysis by thin-layer-chromatograpy/radioautography, and by gas chromatography of derivatized samples. The irradiation source produced 300 nm and longer wavelength ultraviolet light to simulate natural sunlight.

Information Liaison Initials: DRP

FC-143/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-143 in distilled water on exposure to simulated sunlight (Kohler, 1965). This study was conducted essentially as recommended by the Environmental Proection Agency (Federal Register).

EXPERIMENTAL

1. Sample Materials

FC-143 is the ammonium salt of perfluorooctanoic acid.

$$C_7F_{15}COONH_4$$

The major component is the straight-chain C_7 but some branched chain isomers and other homologs also are present.

FC-143 Water Solution.

A 50 ppm solution of FC-143-^{14}C (358 dpm/µg) was prepared by dissolving 140.0 mg of FC-143 in 2.8 liters of distilled water. The resulting solution had a specific activity of 17,320 dpm/ml (0.0078/µC/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

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/methanol/water, 75/15/10
2nd developing solvent-methyl ethyl ketone/chloroform/acetic acid, 55/30/15

X-Ray Film

KODAK NS-2T, 8 x 10 inch size

Gas Chromatography System (GC)

Gas Chromatograph	- Hewlett-Packard Model 5840
Column	- 6 ft 1/8 in od stainless steel packed with 20% DC 200 silicone/10% BENTONE 34 on ANAKROM ABS (100/110 mesh)
Carrier gas	- Argon/methane, 95/5
Column temperature	- 80°C for 4 minute programed to 180 at 5°C/min.
Injection part	- on column, 180°C
Detector	- electron capture, 300°C
Sample injection	- 1 µl via 10 µl microsyringe

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-143 into its corresponding methyl ester just prior to gas chromatographic analysis.

$$C_7F_{15}COOH + CH_2N_2 \longrightarrow C_7F_{15}COOCH_3 + N_2\uparrow$$

(FC-143 acid) (DAM) (FC-143 methyl ester)

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 hydrozide 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 etheral 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 22 ± 2°C by circulating tap water through flexible plastic tubing wrapped around the reaction chamber. Air was passed through the photolysis solution at 10 ml/min for oxygenation and 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, 1, 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). 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 µl aliquot of each sample concentrate (equivalent to 1.0 ml of the original photolyzate solution) was transferred onto a TLC plate using a 10 µl microsyringe. Each plate was developed two-dimensionally, first with ethyl acetate/methanol/water (75/15/10) and then with methyl ethyl ketone/chloroform/acetic acid (55/30/15). 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 plates and LSC. The results are presented in Tables II and III.

6. Investigation for Photoproducts by Gas Chromatography

Perfluorocarboxylic salts as FC-143 are not directly analyzable by gas chromatography but can be analyzed if acidified 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:

> Four ml of photolyzate solution was pipetted into a 4-dram vial and acidified with 0.4 ml of concentrated hydrochloric acid. The resulting samples acids were quantitatively extracted with two 2-ml portions of diethyl ether. The ether extracts were combined in a calibrated 10 ml centrifuge tube. One ml of DAM solution was added and the sample allowed to react for 15 minutes. Excess DAM was then removed by purging the tube contents with a nitrogen jet until the yellow DAM color was almost gone. The sample solution was then diluted to exactly 5 ml with diethyl ether, and analyzed immediately to minimize possible degradation due to any instability of the sample derivative.

The chromatograms for the 30 and 0-day photolyzate samples are presented in Figure 4.

However several less obvious parameters are important: The DAM soultion should be freshly prepared, preferably the same day it is used. Several injections of sample may be necessary to passivate the column before accurate and repeatable results are obtained.

RESULTS

No photodegradation of FC-143 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.

The 30 and 0-day photolyzates had similar radiocarbon assays (Tables II and III) so no significant amount of radiocarbon was volatilized during the photolysis and so the contents of the vapor trap were not analyzed. Radiocarbon recoveries after sample concentration were good for the 30-day photolyzate (99%) but less desirable for the 0-day sample dure to physical loss (86%). A repeat concentration of the 0-day sample was not done since it is important only as a TLC reference.

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

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

J. W. Todd

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.

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

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

General Electric Company, Lamp Division, Cleveland, OH 44112.

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

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

Figure 1 - Photoreactor

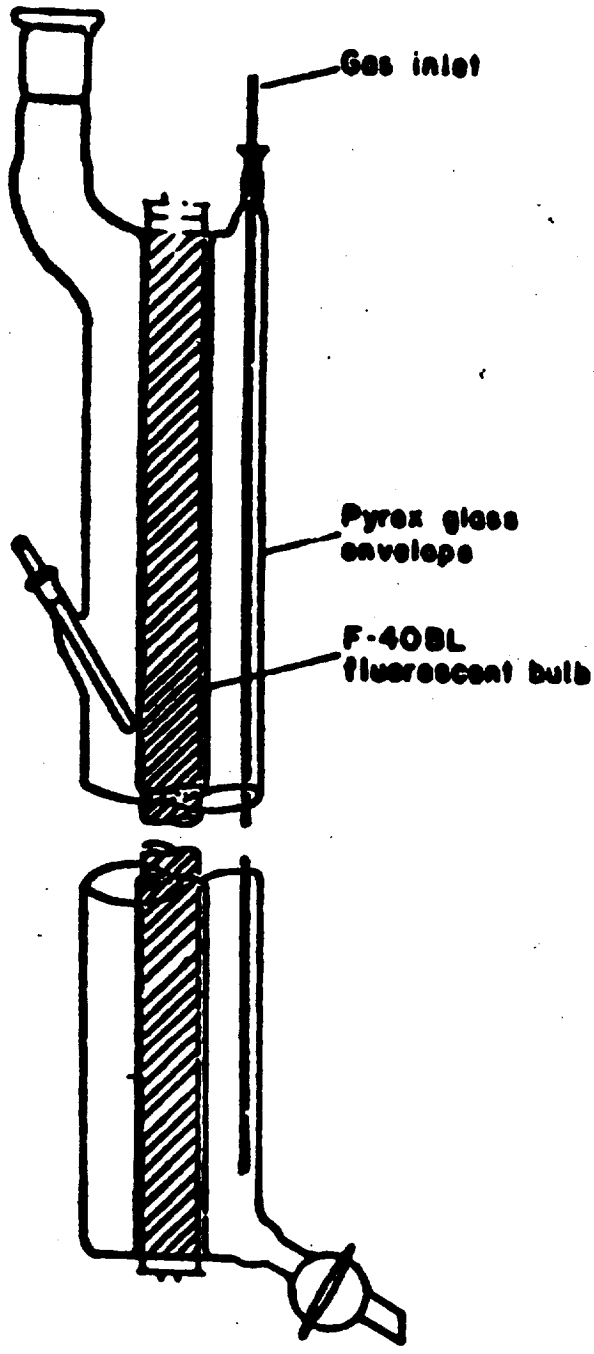


Table I - Spectral Energy Distribution for a GE F40BL Black Light Bulb

Wavelength	Watts Radiated	
290 - 300	0.090	
310 - 320	0.235	
320 - 340	1.410	
340 - 360	1.910	Maximum intensity at about 360 nm
360 - 380	2.310	
380 - 400	1.680	
400 - 500	2.300	
500 - 600	0.340	

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

Sample Solution		TLC Plate Scrapings			
DPM/ml	Relative %	Area	Description	DPM(per ml)*	% Recovery
17,320	[100]	1	FC-143	16,643	97
		2	Origin.	66	0.4
		3	"Background"	288	1.7
			Total	16,997	99.1

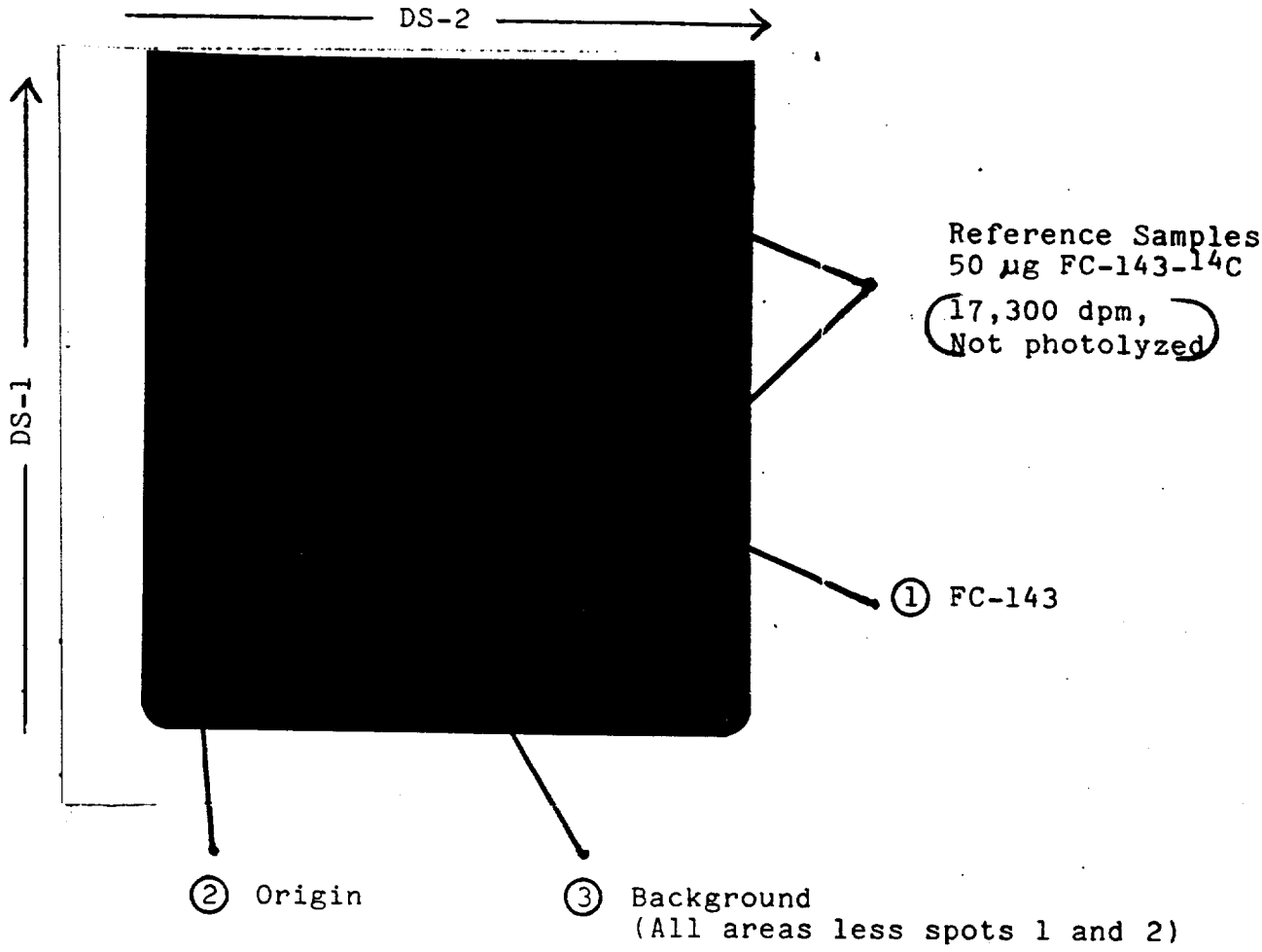
* The amount of ^{14}C radioactivity on the plate is equivalent to 1 ml of the original photolyzate solution.

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

Sample Solution		TLC Plate Scrapings			
DPM/ml	Relative %	Area	Description	DPM(per ml)*	% Recovery
16,643	[100]	1	FC-143	14,493	84
		2	Origin.	43	0.2
		3	"Background"	222	1.3
			Total	14,758	85.5

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

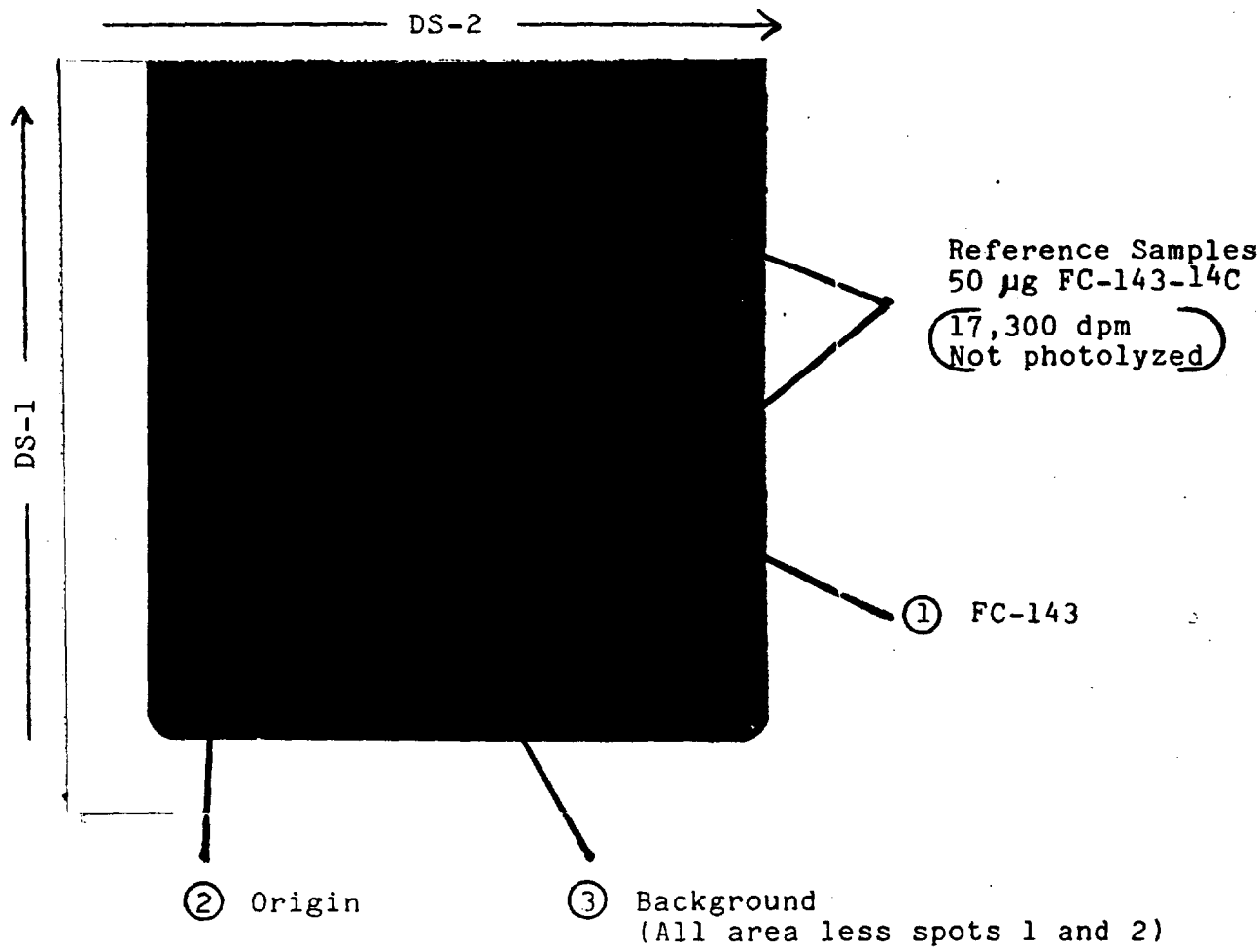
Figure 2 - Photograph of TLC Radioautograph
30 Day FC-143 Photolyzate



DS-1 = Developing Solvent #1, ethyl acetate/methanol/water, 75/15/10

DS-2 = Developing Solvent #2, methyl ethyl ketone/chloroform/acetic acid, 55/30/15

Fgiure 3 - Photograph of TLC Radioautograph
0-Day FC-143 Photolyzate



DS-1 = Developing Solvent #1, ethyl acetate/methanol/water, 75/15/10

DS-2 = Developing Solvent #2, methyl ethyl ketone/chloroform/acetic acid, 55/30/15

Figure 4 - Gas Chromatogram of Derivatized Photolyzate Samples