

AR226-0365

OTHER AVAILABLE STUDY SUMMARIES FOR N-EtFOSE ALCOHOL

TEST SUBSTANCE

Identity: N-ethylperfluorooctane sulfonamidoethanol; may also be referred to as N-EtFOSE Alcohol or FM-3422. (1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-, CAS # 1691-99-2)

Remarks: Material is an off-white, waxy solid of uncharacterized purity.

The attached are overviews created from 1983 and before. Robust summaries are being submitted for many of the individual studies covered in these reviews. Others have not been summarized due to the fact new studies exist that supercede these, the original study cannot be found, or they are being repeated.

OTHER

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TECHNICAL REPORT SUMMARY

Date
11/15/77

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

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Division	Environmental Laboratory (EE & PC)	Dept. Number	0222
Project	Fate of Fluorochemicals	Project Number	9970612643
Report Title	Analytical Methodology on FM 3422	Report Number	8
To	D. L. Bacon		
Author(s)	A. Mendel	Employee Number(s)	43939
Notebook Reference		No. of Pages Including Coversheet	13

SECURITY ►

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(Company Confidential)☐ Closed
(Special Authorization)3M CHEMICAL
REGISTRY ►New Chemicals Reported
☐ Yes ☒ No

KEYWORDS:

(Select terms from 3M
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applicable terms.)EE & PC-Div.
Fluorochemical
Analytical

CURRENT OBJECTIVE:

Progress Report

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

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INTRODUCTION

This portion of the report was concerned with the analytical aspects of FM 3422. It was quantitated by gas chromatography (GC) using electron capture detection. Before analyses could be conducted, however, many variables had to be resolved and some experimental observations needed clarification. These are discussed below and detailed in the experimental section.

DISCUSSION AND RESULTS

The solvent of choice for extraction of FM 3422 from water was ethyl acetate, since recent literature studies have indicated ethyl acetate to be superior in general to ether. The recovery of FM 3422 by ester extraction was quantitative from water and from water to which salt (salt-out technique) was added respectively. FM 3422 can be quantitated up to at least 125 ppm (region of linearity; see Figure 1). Solutions of FM 3422 above this concentration (e.g., 250 ppm), gave responses beyond the integrator's range. The limit of detection was found to be 0.05 ppm which represents 0.25 ng absolute. Naturally, solutions of FM 3422 higher or lower in concentration can be diluted or concentrated respectively for analysis in the range of linearity.

The gas chromatographic pattern for FM 3422 was examined briefly and is shown in Figure 2. While the Carbowax 20M column used in this study resolves the product into three peaks, other columns (e.g., OV101, SE52, W982) may not all resolve FM 3422 into three components (1).

The solubility of FM 3422 in water was determined to be 0.05 ppm using a recently designed apparatus for continuously saturating water with hydrophobic organic chemicals (2).

Concentration of FM 3422 from water (rotary evaporator) gave low recoveries. Concentrations can be conducted successfully from organic solvents provided water is absent or that water has been removed previously by forming an azeotrope. This same observation was noted independently for another fluorine-containing compound(3).

It was also necessary to determine the kind of containers that could be used to hold FM 3422 containing samples which would be generated in soil and aquatic testing studies. Plastics such as polyethylene and polycarbonate were unsatisfactory, while glass was satisfactory at the 0.05 ppm concentration of FM 3422 in water. These results are shown in Table IV.

Stability of FM 3422 to alkali was also studied. In 20% alcoholic potassium hydroxide at 50°, thirty percent of the FM 3422 hydrolyzed after seven hours and after twenty-four hours, only eight percent FM 3422 remained (see Table V). TLC and IR studies of these products showed that FM 3422 was converted to FC-95 as expected.

The ability of sludge (bacteria) to biodegrade FM 3422 was also investigated. If FM 3422 biodegrades, theoretically, it might degrade to perfluorooctane sulfonamide and/or to FC-128 (N-perfluorooctanesulfonyl-N-ethylglycine or a salt thereof). It was necessary to show that neither of these materials interfered with the GC analysis of FM 3422. This was the case.

Radioactive FM 3422 (labeled in the R_f group) was also used in biodegradation studies described elsewhere in this report. Preliminary TLC (thin-layer chromatography) and subsequent autoradiography revealed the sample to be impure. Accordingly, it was purified by a combination of preparative TLC and column adsorption chromatography to give FM 3422-¹⁴C whose autoradiogram showed one spot only.

Die-away studies to measure the biodegradation, if any, of FM 3422 are discussed in a different section of this report. In this section of the report, however, the ethyl acetate extracts from these die-away studies were routinely examined by TLC, which showed a second spot in addition to expected FM 3422. Scaleup (preparative TLC) afforded enough of this second component for IR, mass spectroscopy (MS) and GC studies. IR indicated a fluorocarbon species complexed possibly with a nitrogen-containing compound. MS showed FM 3422 plus carbon dioxide and ammonia and GC revealed only FM 3422. This second component was not further characterized.

Analytical methods to quantify FC-95 directly are not known. Some scouting time was devoted to try to derivatize FC-95 so that the derivative could be analyzed. Summarized below are methods which have failed.

Sulfonates are known to form complexes with benzyl isothioureahydrochloride by displacement of the chloride with the sulfonate anion. Accordingly, the crystalline trifluoromethanesulfonate of the UV-absorbing benzyl isothioureahydrochloride was synthesized (41433-49). Unfortunately, this complex was not stable in aqueous solution (sulfide odors) and it did not lend itself to analysis by HPLC using UV detection, or by fluorescence (very weak fluorescence).

FC-95 could not be caused to react with 2,4-dinitrofluorobenzene (44191-25) nor could the phenyl ester be made by esterification with phenol-boric acid-sulfuric acid (44191-33). FC-95 could not be converted to the sulfonyl chloride using phosphorus oxytrichloride in pyridine (44191-35).

Perfluorooctane sulfonic acid could not be caused to condense with aniline in the presence of dicyclohexyl carbodiimide, a potent water scavenger (44191-36, -38).

EXPERIMENTAL (4)

This work is recorded in notebooks 41433, 41947, 44191, and 46269, and filed under Environmental Laboratory Request 3645.

FM 3422 (labeled E788, CG745-2 and received from D. Ricker, Commercial Chemicals) was off color and accordingly was sublimed (60°/ <1 mm Hg) to give white solid which was used in subsequent work unless indicated otherwise. All solvents used were reagent grade. Thin-layer chromatography was performed on silica gel coated on glass plates (E. Merck) and plate visualization was performed according to the "Wong" technique, described in notebook 44191-16, -17-20, -21, -22.

FM 3422 was gas-chromatographed using the HP Model 5713 GC with the Model 3380A integrator-printer. GC conditions were: Carbowax 20M column, 6% loading on Q support (column 0.18m x 3.18mm; 6 foot x 1/8 inch O.D.); injection port, 200°C; detector, 300°C; column isothermal, 170°; argon/methane flow rate about 40 ml/min.

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GAS CHROMATOGRAPHY OF FM 3422

Comparison of Nonsublimed with Sublimed FM 3422 (41947-26)

A 10 ppm solution in 1-octanol of FM 3422, crude and sublimed respectively, was gas chromatographed. The area percents were compared and the sublimed material was shown to be purer, i.e., the nonsublimed material was 9.94 ppm, based on the sublimed material being 10 ppm. GC program: initial temperature, 170°; final temperature, 210° at 8°/min.

Determination of Linear Range of Detection of FM 3422 by EC/GC

A standard solution of 1000 ppm of FM 3422 was diluted to give 250-, 125-, 100-, 50-, 25-, 20-, and 10- ppm solutions. Five microliter aliquots were then injected into the GC and the RESPONSE (area) was recorded. The data are given in TABLE I and illustrated in Figure 1.

TABLE I

DETECTION LIMITS OF FM 3422

<u>Standard Solution (ppm)</u>	<u>RESPONSE (Area)</u>	<u>Area x 10⁶</u>
1000	*	
250	*	
125	18,534,286	18.5
100	14,741,274	14.7
50	7,502,012	7.5
25	3,819,671	3.8
20	3,138,201	3.1
10	1,598,396	1.6

*Beyond signal response of integrator.

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AREA UNITS ($\times 10^6$)

0

2

4

6

8

10

12

14

16

18

20

20

40

CONCENTRATION (ppm)

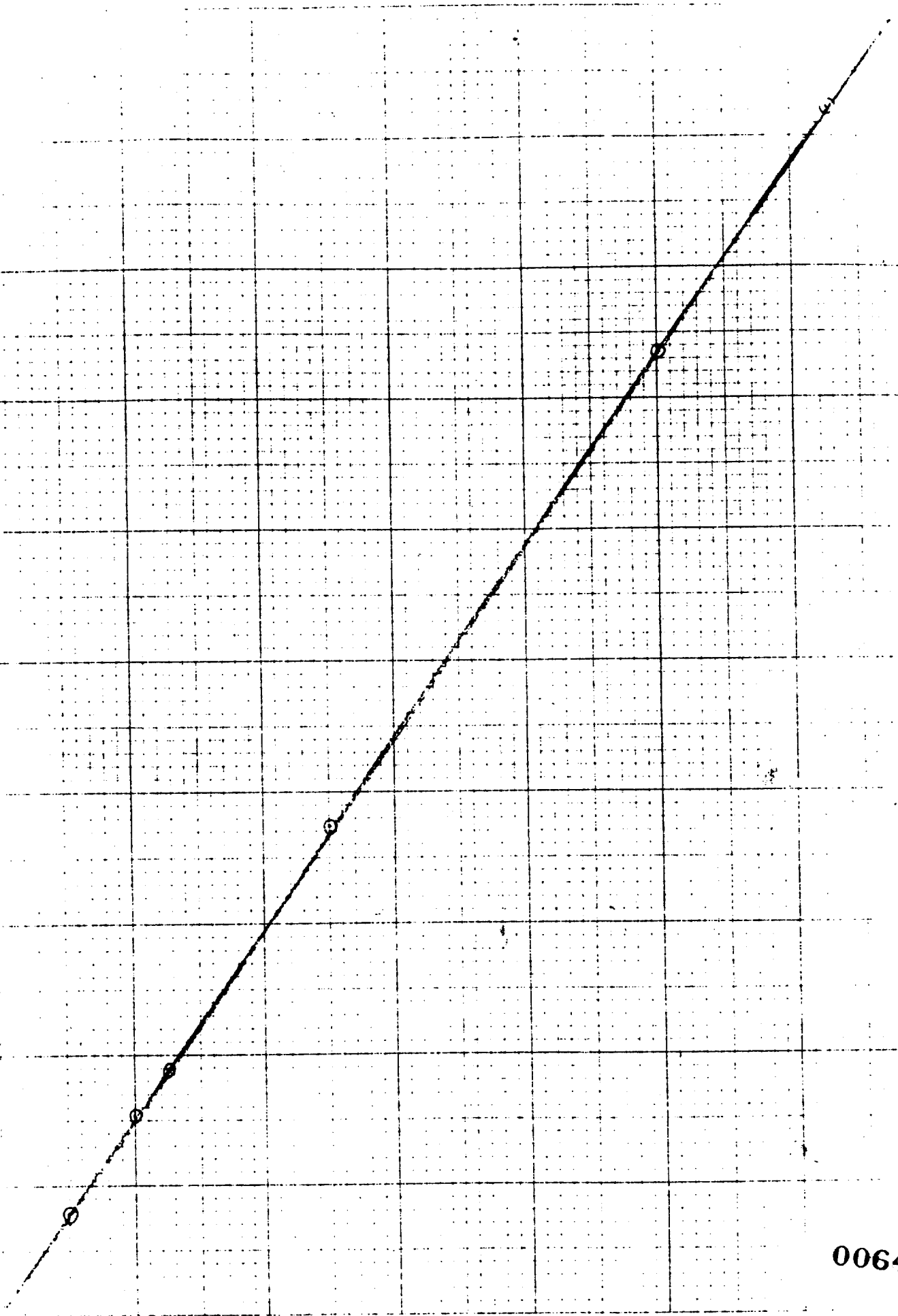
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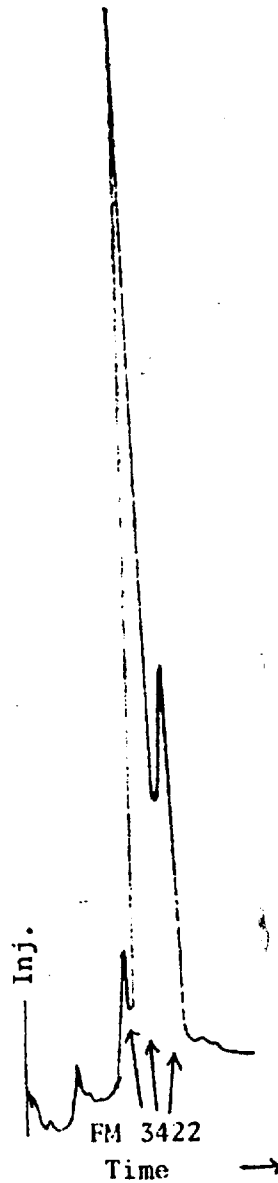
120

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Figure 1 - Range of Detection of FM 3422





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Figure 2

GAS CHROMATOGRAPHIC
PATTERN OF FM 3422

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EXPERIMENTS ON THE RECOVERY OF FM 3422

A. Recovery of FM 3422 from Ethyl Acetate: (41947-42)

Ethyl acetate (ca. 1 ℓ) was stored over anhydrous sodium sulfate and used as needed. A 500 ppm standard of FM 3422 in ethyl acetate was prepared by weighing 0.050 g. of FM 3422 and diluting it to the mark (100 ml) in a volumetric flask. Similarly, a 25 ppm solution was prepared by pipetting 5 ml of the above solution into a 100 ml volumetric flask and diluting it to the mark.

To make sure that the FM 3422 in dry ethyl acetate was not lost by evaporation, 10 ml of the 25 ppm standard was pipetted into a 10 ml volumetric flask. A slow stream of nitrogen was used to evaporate the ethyl acetate and an aliquot was gas chromatographed. Comparison of GC results with the original 25 ppm solution showed a recovery of 99.99 percent.

B. Recovery of FM 3422 from Ethyl Acetate-Water and from Ethyl Acetate-Salt Water (41947-45)

It was anticipated that in future experiments involving the preferential extraction of FM 3422 from aqueous media and from media containing biological components, e.g., fish, sludge, soil, and the like, it might become necessary to use saturated sodium chloride ("salt-out" technique) for two reasons: to increase transfer of FM 3422 from aqueous media into ethyl acetate; to help prevent the potential emulsions which ethyl acetate appears to form with many biological ingredients.

Accordingly, 25 ml of 25 ppm FM 3422 in ethyl acetate was pipetted into 25 ml of water, and into 25 ml of water containing 5 ml of saturated sodium chloride, respectively. Each mixture was shaken in a separatory funnel (fifty inversions respectively) and the respective ethyl acetate layer was analyzed by gas chromatography. The results are shown in TABLE II.

TABLE II
RECOVERY OF FM 3422

<u>Experiment</u>	<u>Description</u>	<u>Vol. EtOAc Recovered (ml)</u>	<u>GC INTEGRATOR RESPONSE (AREA)</u>	<u>FM 3422 (ppm)</u>
1	25 ppm FM 3422 (in EtOAc)	Standard Solution (25 ml)	4,337,111	25
2	25 ml FM 3422 + 25 ml Water	23.5	4,363,283	25.15
3	25 ml FM 3422 + 25 ml water + 5 ml Sat'd NaCl	24.5	4,325,514	24.93

Note that the addition of salt water allowed approximately 1 ml more of ethyl acetate to be separated compared to water, i.e., the FM 3422 is now in 24.5 ml of ethyl acetate whereas before (not using salt-out techniques) the FM 3422 was in 23.5 ml of ethyl acetate. This explains why the result in experiment 3 is slightly lower than that in experiment 2. Nevertheless, no loss is noted using the salt-out technique. A volume correction factor may be needed, however.

C. Recovery of FM 3422 from Water (41947-38, 39, 40)

During experiments to determine the distribution coefficient of FM 3422 between 1-octanol and water, the water phase was separated and quantitatively transferred to a flask. It was rotary evaporated (50°/water aspirator pressure, 20 mm Hg) to remove water. The residue was taken up in a known volume of 1-octanol and an aliquot was gas chromatographed. Results were low indicating that FM 3422 was lost by sublimation and/or by steam distillation.

Accordingly, the all glass-to-teflon lining in the rotary evaporator was leached with a small amount of methanol. A small portion of this leaching was gas chromatographed and the results showed the presence of FM 3422.

Finally, the water condensate, collected during the rotary stripping, was extracted with a small amount of 1-octanol. Gas chromatography of the separated 1-octanol extract again showed the presence of FM 3422. It appears therefore that unless all the water is removed from FM 3422-water mixtures by azeotropic distillation or by a drying agent, results will be low in FM 3422. Consultation with other workers (3) indicated that similar problems were observed with other fluorine-containing compounds. Removal of water by azeotropic distillation or by evaporation with an excess of solvent, such as ethyl acetate, solved the recovery problem.

DETERMINATION OF SOLUBILITY OF FM 3422 IN WATER

The Veith-Comstock technique (2) was used for this experiment.

Glass beads (ca. 300 g, 3 mm. in diameter) were added to a solution of 100 mg of FM 3422 in about 500 ml of acetone. The solvent was allowed to evaporate, thus depositing the fluorochemical on the beads. The beads were packed into a column (ca. 25 mm. dia. x 450 mm.) whose end was prepacked with a 20 mm. layer of silanized glass wool, followed by a 20 mm. layer of sand.

The top of the column, packed with a 20 mm. layer of silanized glass wool, was attached by Mayon^(R) tubing to the top inlet of a 2-liter bottle filled with water. The bottom of the column was attached by tubing through a peristaltic pump, to the bottom outlet of the 2-liter flask. The water was circulated upwards by the pump through the column for about two weeks. By volumetric pipet, one hundred milliliters of saturated liquid was withdrawn, diluted with 10 ml of aqueous saturated salt, and extracted 3 times with a total of 21 ml of ethyl acetate. The combined extract was diluted to 25 ml (volumetric flask). An aliquot was gas-chromatographed. This experiment was performed eight times. The results are reported in TABLE III.

TABLE III

SOLUBILITY OF FM 3422 IN WATER*

<u>Experiment No.</u>	<u>ppm FM 3422</u>
1	0.050
2	0.045
3	0.061
4	0.042
5	0.040
6	0.062
7	0.050
8	0.048
Mean	0.04975

*Temp. = 20° C.

Mean = 0.05 ppm; Range = 0.04-0.062 ppm; Std. Dev. = 0.0084

RECOVERY STUDIES OF AQUEOUS FM 3422 SOLUTIONS IN VARIOUS CONTAINERS (44191-42)

At the low solubility level of FM 3422 in water (0.05 ppm), the possibility was considered of incomplete recoveries due to sorption of FM 3422 by plastics and/or glass. Accordingly, the following study was made:

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One hundred milliliters of 0.05 ppm FM 3422 in water (by the Veith-Comstock technique (2) as described earlier) was added to an amber glass - and to a polyethylene - container, respectively. The containers were capped and allowed to stand in the laboratory for one week. The respective contents of the containers were transferred quantitatively to a separatory funnel. The container was rinsed with two milliliters of water only. To the funnel was added 10 ml of saturated aqueous sodium chloride and 19 ml of ethyl acetate. The contents were extracted and the organic extract was transferred quantitatively to a 25 ml volumetric flask. The aqueous phase was re-extracted twice with 5 ml of ethyl acetate. The combined organic extract was diluted to the mark (ethyl acetate) and then gas chromatographed.

To each of the now empty containers used above was added (pipet) 1 ml of methanol. The respective container was sealed, rinsed with this 1 ml of methanol, and an aliquot was gas chromatographed. Experiments were performed in duplicate and the results are indicated in TABLE IV.

TABLE IV
CONTAINER STUDIES WITH FM 3422

<u>Experiment No.</u>	<u>Container</u>	<u>FM 3422 in 100 ml water (μg)</u>	<u>Total FM 3422 in Container: Meth- anol Rinse (μg)</u>	<u>Total FM 3422 Recovered* (μg)</u>
1	Glass	5.8	0.04	5.8
2	Glass	4.6	0.19	4.8
3	Polyethylene	<3	1.88	<4.9
4	Polyethylene	<3	1.15	<4.2

*Solubility of FM 3422 in water determined as 0.05 ppm or 5 μ g/100 ml.

It appears therefore that glass containers may be used but polyethylene must not be used to store solutions at these concentrations; otherwise, severe losses of material are possible.

ALKALINE HYDROLYSIS OF FM 3422

The stability or instability of FM 3422 toward base was apparently studied several years ago under aqueous conditions. Because this material steam distills and because of its lack of water solubility, the stability of FM 3422 toward base in alcohol was studied in the present work as follows:

Six samples each of a 25 ml solution of 362 ppm of FM 3422 in 20% alcoholic potassium hydroxide was kept in a 50° oil bath for varying lengths of time. A sample was taken after 0.5-, 1-, 7- and 24- hrs., and neutralized with concentrated nitric acid to the phenolphthalein indicator end point; this allows precipitation of potassium nitrate and minimizes water which tends to interfere with the EC/GC analyses. GC analysis of the alcohol solution gave the results in TABLE V.

TABLE V

HYDROLYSIS STUDIES OF FM 3422

Time (in hrs.)	0	0.5	1	7	24
3422 (in ppm)	362	380	362	256	28

A sixth sample was allowed to remain in the oil bath for 50 hrs/50° C. It was neutralized as above and filtered to remove solids. The filtrate was concentrated to dryness and the residue was analyzed by TLC, and IR and NMR (Req. C46749). A comparison of the R_f value of the residue with that of authentic FC-95 showed they were the same. IR and NMR studies confirmed that the FM 3422 was broken down to FC-95 under these conditions.

GAS CHROMATOGRAPHY OF PERFLUOROOCCTANE SULFONAMIDE AND FC-128 (41947-48)

The retention time of FM 3422 was 2.8 minutes isothermal at 160° using the conditions described earlier. To determine whether the above sulfonamide and FC-128 posed as an interference to FM 3422, dilute solutions (in methanol) were made for these two materials. The sulfonamide could be chromatographed isothermally at 200° (about 3.3 minutes retention) while FC-128 could not be chromatographed. Therefore, there is no interference problem.

THIN-LAYER CHROMATOGRAPHY STUDIES OF FM 3422

Radiolabeled FM 3422 (5) was examined by TLC for purity. About ten micrograms of sample was spotted on a plate which was then developed in ethyl acetate. The plate was exposed to an X-ray film for about one week and the film was developed. It revealed that the FM 3422-¹⁴C had three impurities, two components of greater R_f and one component remaining at the origin. Accordingly, the entire radioactive material, nearly 1.7 g, was column chromatographed on silica gel by chloroform elution. About forty 15 ml fractions were collected and monitored by TLC-auto¹⁴ radiography. Pure material was combined for future studies. Impure FM 3422-¹⁴C was combined and rechromatographed as above until essentially all of the material was rendered pure (6).

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The visualization technique for nonradioactive fluorochemicals was described in notebook 44191-16-17, 20-22, and in TAG (7). Briefly, the developed, dry TLC plate is sprayed with chloroplatinic acid according to Wong (8). The dry plate is then carefully sprayed with 1% aqueous starch solution until the plate is wet but not runny or soaked. The wet plate is then placed in an iodine chamber for about two minutes and examined. Fluorochemicals (and as it turns out, most chemical in general) are visualized as a white or white-to-pink spot against a dark purple background. This contrasting dark purple color will fade with time so that after about 1 hour, a faint pink-to-white spot will be noted against a light violet background. This color, however, remains stable for months and supersedes any visualization reagents to date. Between 0.1 and 1 microgram absolute of FM 3422 has been detected routinely.

TLC STUDIES ON DIE-AWAY EXPERIMENTS (44191-27-32)

Die-away studies on mixtures of FM 3422 with activated sludge-Alcanox^(R) (commercial surfactant) - YM broth-buffer-mixtures are detailed in another report (E. A. Reiner). The final experiments were quantitatively extracted with ethyl acetate for further examination by GC for FM 3422 and by TLC evaluation for any materials not capable of being detected by GC (i.e., non-volatile materials).

Ethyl acetate extracts of seven samples from die-away experiments (labeled 18AT; 3422 #2; 61AT, 3422 Day 0; 61ATC, #1; 61AT, 3422 #2; 25 SIAT, 3422 final; 34 SAT, 3422 final; 25 SIAT, 3422 Day 0 and a reference composite containing known FM 3422 and known FC-95) were spotted on one TLC plate. It was confirmed by earlier GC studies that those samples labeled day 0 had about 500-600 ppm of FM 3422, while those samples that had been carried through biodegradation studies had considerably less (one-fifth or less) FM 3422 remaining. The TLC plate was developed (ethyl acetate) and visualized in the usual manner. Extracts from samples 61ATC #1, 61AT, 3422 #2, and 25 SIAT, 3422 final, had small amounts of FM 3422, plus a new component whose R_f value (0.45) was just below that of FM 3422 (0.52). Accordingly, these last three extracts were combined and twice preparatively thin-layer chromatographed using five developments in chloroform each to effect a complete separation between FM 3422 and the desired new material. Work up of the desired preparative layer by acetone extraction afforded about 5 mg of a semisolid which was found to be less readily soluble in methanol than FM 3422. This semisolid was examined by IR (CRL Req. C47334, C47442) which suggested a complex between FM 3422 and an unknown. Mass spectroscopy (Req. C 47585) indicated FM 3422, plus ammonia, plus carbon dioxide. GC of this complex indicated FM 3422 only. Two nonrelated materials isolated in the course of this preparative TLC study were glycerin and fatty acid, both of which probably arose from biodegradation of the YM broth, an added nutrient for the sludge.

Based on IR studies, a possible candidate as the complexing agent with FM 3422 was urea (9). Recall that the complex mass spectrum indicated FM 3422, ammonia, and carbon dioxide. Accordingly, a mixture of urea and FM 3422 in methanol and in acetonitrile was reflexed for several hours and examined by IR which suggested a physical mixture of the two components, respectively (44191-41). This complex was not further characterized.

Charles Reider

AM/cen

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- (2) G. D. Veith and V. M. Comstock, J. Fish Res. Board Can., 32, 1849 (1975).
- (3) C. D. Green (Commercial Chemicals) communication with A. Mendel.
- (4) Much of the experimental work was performed by G. Vraspir and C. Schrandt.
- (5) Received from D. McCown (Commercial Chemicals).
- (6) Autoradiography and X-ray film development was performed in the Agricultural Chemicals Laboratories (Commercial Chemical). The help of Agrichem personnel is acknowledged.
- (7) 3M Technical Awareness Gazette (TAG), 6, No. 5, 3231 (1977).
- (8) F. F. Wong, J. Chromatography, 59, 448 (1971).
- (9) J. J. McBrady (Central Research Laboratories, Molecular Spectroscopy) communication with A. Mendel.



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TECHNICAL REPORT SUMMARY

Date
1/17/79

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

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

Division	Environmental Laboratory (EE & PC)	Dept. Number	0535
Project	Fate of Fluorochemicals	Project Number	9970612643
Report Title	Analytical Methodology and Support	Report Number	008
To	D. L. Bacon		
Author(s)	Arthur Mendel	Employee Number(s)	043939
Notebook Reference	41947, 44191, 46269, 47703, 48277, 49400	No. of Pages Including Coversheet	22
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.)

EE & PC-Div.
Fluorochemicals

CURRENT OBJECTIVE:

Progress Report

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

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INTRODUCTION

This report describes supporting analytical work not detailed in reports on bioassay, die-away, soil absorption-desorption, solubility, and the like on various fluorochemicals.

DISCUSSION AND RESULTS

The loss of FM 3422 on rotary evaporation of its water solutions was noted previously (1), and only ten percent of FM 3422 was recovered; see the experimental section of this report for details. In another experiment, a water solution of FM 3422 was allowed to evaporate under ambient conditions with essentially complete loss of FM 3422. Interestingly, similar losses of PCB's in water due to volatilization were reported (2). Note that the solubility of PCB's in water is very similar to that of FM 3422 (around 1 ppm or less). In the case of PCB's, volatilization was minimized by working in a cool environment and covering samples with a layer of hexane.

The distribution coefficient for FM 3422 was reported earlier (3), wherein the solubility of FM 3422 in water was not completely defined but based on experimental work, thought to be less than 0.05 ppm. This value was based on water solutions filtered through various size membranes and examining the aqueous filtrate with a light beam (Tyndall effect). It is known that membrane filters contain impurities which may interfere by removing a substrate in water or otherwise contaminating the water (4,5). The solubility of FM 3422 in water using the Veith technique (6) was calculated to be 0.05 ppm, and the distribution coefficient for FM 3422 is thus $330,000 \text{ ppm}$ (in n-octanol) divided by 0.05 ppm (in water) or $P = 6.6 \times 10^6$.

N-alkyl-substituted perfluorooctanesulfonamides have been shown to undergo alkaline and acidic hydrolysis; however, the reaction takes days (7). A pilot study on the basic ethanolysis of FM 3422 also confirmed that this substrate is not rapidly degraded (46269-45) and that the salt of perfluorooctanesulfonic acid was formed (infrared and TLC studies). Accordingly, a kinetic study was conducted on FM 3422 using 10% potassium hydroxide in absolute ethanol (to ensure complete solution). The reaction rate obeyed first order kinetics with a rate constant $K = 9 \times 10^{-3} \text{ hr}^{-1}$ and a half life of seventy-seven hours.

In earlier studies (8), glass containers were shown to be satisfactory for the quantitative recovery of FM 3422 from water in the parts per million (ppm) or less concentration range. In the current work, similar aqueous solutions of FC-95 could be kept in polypropylene, but not in polyethylene, polycarbonate, or glass. Aqueous solutions of FC-143 could be kept in polypropylene; polyethylene and glass were less suitable. These studies were done with radioactive compounds (see experimental).

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Based on studies to date, it appears that compounds such as FC-95 and FC-143, which have highly ionizable groups adhere to glass (which may be considered to have an ionic surface) but not to plastic (hydrocarbon or nonionic surface). For quantitative recoveries then, such compounds should be stored in plastic containers. On the other hand, nonpolar compounds, such as FM 3422, adhere (dissolve?) to plastic but not to glass, and the latter would be the container of choice. Another rationale involves the distribution coefficient. Samples which have a high distribution coefficient (i.e., are very lipophilic) would prefer to adhere (dissolve?) to plastic compared to glass (so use glass containers), while samples which have a low distribution coefficient (i.e., are very hydrophilic) would prefer to adhere to glass compared to plastic (so use plastic containers).

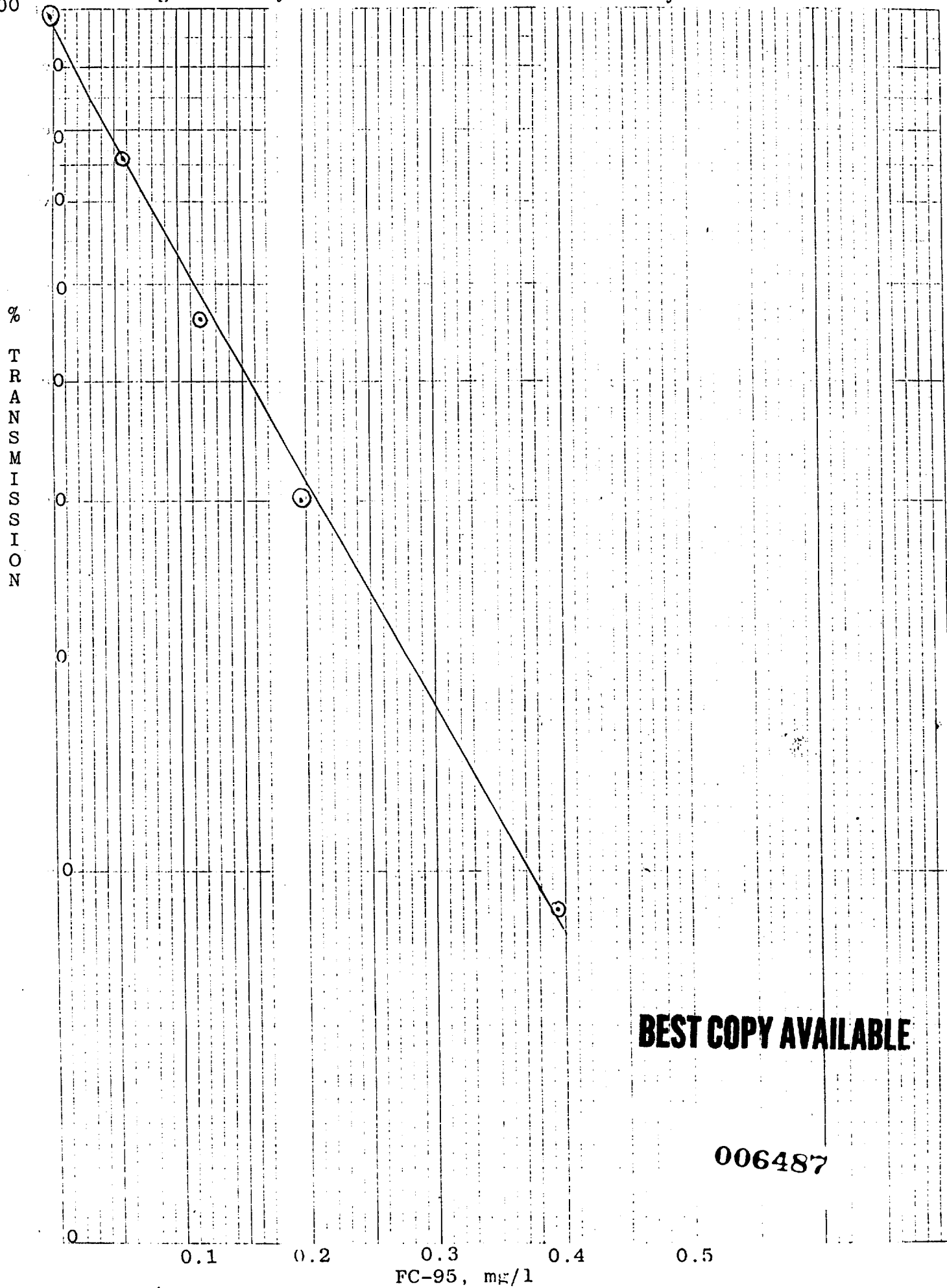
The use of the proper aquaria (glass or plastic) and the most suitable containers for shipping water samples and fish back to the Environmental Laboratory for further analyses was made known to Bionomics Laboratory personnel before they conducted critical life stage studies on FC-95, FC-143, and FM 3422. Aluminum foil-lined caps, used to seal bottles containing aqueous solutions of FM 3422, were also examined before use for possible contaminants that might interfere with subsequent GC analyses; no interferences were observed.

Since a simple, rapid method for quantitation of FC-95 is still not available, the methylene blue procedure for methylene blue active substances (MBAS, (10)) was used to quantitate FC-95. A linear range from 0.4 to 0.06 ppm was noted on semilog paper (Figure 1). Of course, MBAS, such as linear alkyl sulfonates (detergents), if present, will give a positive interference.

TLC and GC were also performed on die-away experiments with radio-labeled FC-95 and FC-143. Die-away samples were spotted directly on E. Merck silica gel TLC plates which were then developed and visualized by autoradiography. A comparison with controls showed no new compounds were formed respectively. Samples including controls were methylated and gas chromatographed to see if any new volatile materials were generated but none were observed in either case. GC of the samples prior to methylation also indicated that no new compounds were formed in each case.

Chiou and co-workers (9) published an article which described an empirical equation relating experimental n-octanol/water distribution coefficients to aqueous solubilities of many organic materials. Their correlation, which covered more than eight orders of magnitude in solubility (from 10^{-3} to 10^4 ppm) and six orders of magnitude in distribution coefficient (from 10 to 10^7), may allow an assessment of distribution coefficient from solubility with a predicted error of less than one order of magnitude. Furthermore, these workers observed a correlation between the bioconcentration factors in

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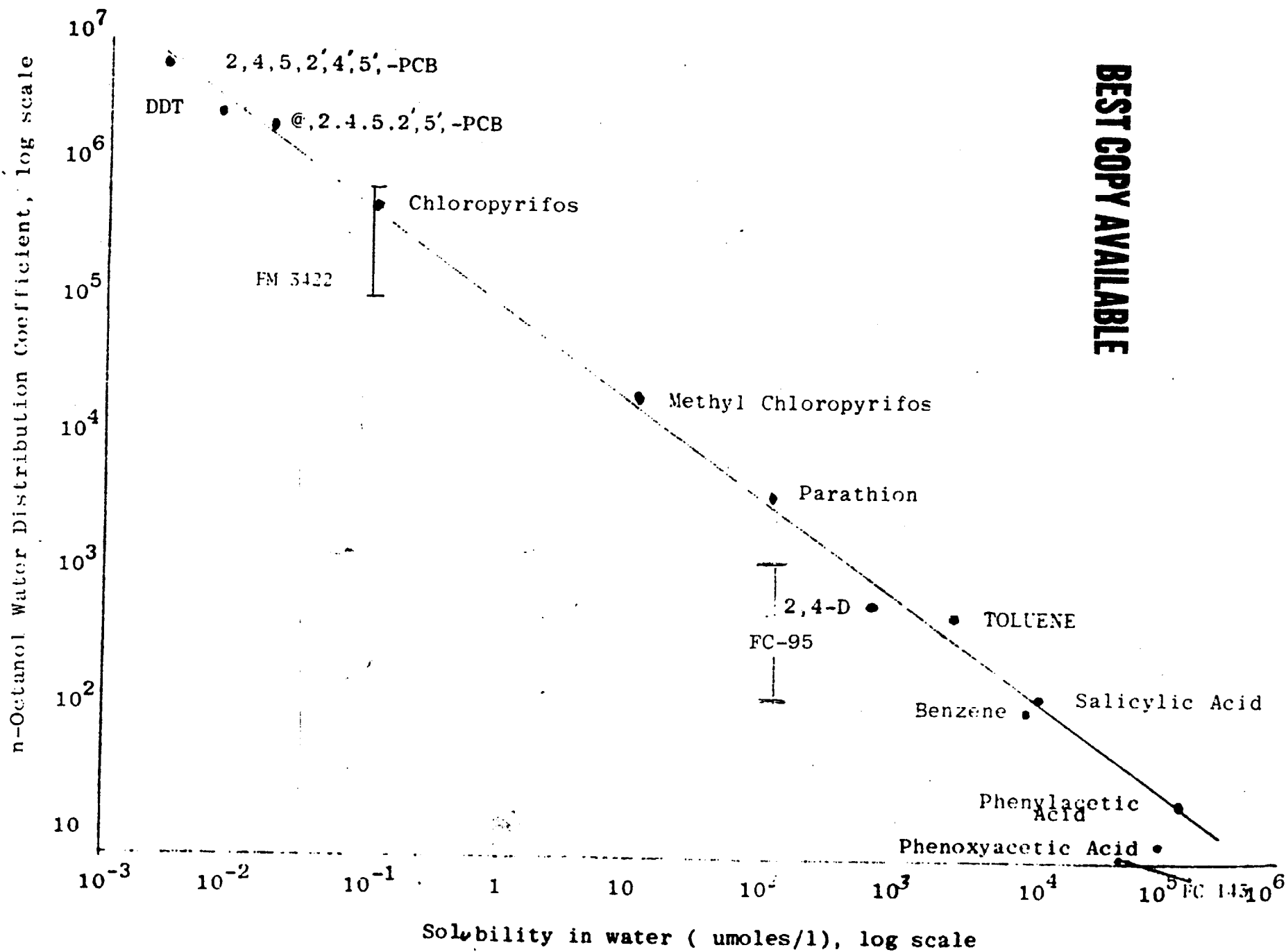
rainbow trout and the aqueous solubilities for some stable organic compounds. It was of interest to apply their empirical equations to solubility, bioconcentration factor, and distribution coefficient data obtained in the Environmental Laboratory on FM 3422, FC-95, and FC-143. Results are summarized in Figures 2 and 3 (11).

Soil thin-layer chromatography (soil TLC) of pesticides appears to offer a simple, yet reliable, method of evaluating relative mobility in soils, even though a universal "standard" soil has not been designated. The advantages of soil TLC include rapidity, reproducibility, and low equipment costs.

In the current study, a soil-coated TLC plate was spotted with radiolabeled FM 3422, FC-95, and FC-143, and the ascending water-developed plate was visualized by autoradiography. Results show that none of the samples appear to migrate ($R_f=0$). Soil TLC in the descending development mode will be done to simulate the leaching of materials through soil.

To date, no evidence has been noted for the biodegradation of FM 3422. It was thought that electrochemical oxidation (voltammetry) might be successful. If so, the potential required would be an indication of the ease or difficulty of oxidation of this alcohol to the aldehyde and/or acid. Furthermore, it was hoped that voltammetry (*i.e.*, oxidation potential) might be a good general physical-chemical predictor of the biodegradation of a candidate. In this work, FM 3422 in acetonitrile was not oxidized by electrochemical procedures using a platinum electrode. Under the same conditions, n-butanol was not oxidized either (CRL Req. B34247). It appears that this method is probably not a good index for the "oxidation potential" of a candidate organic.

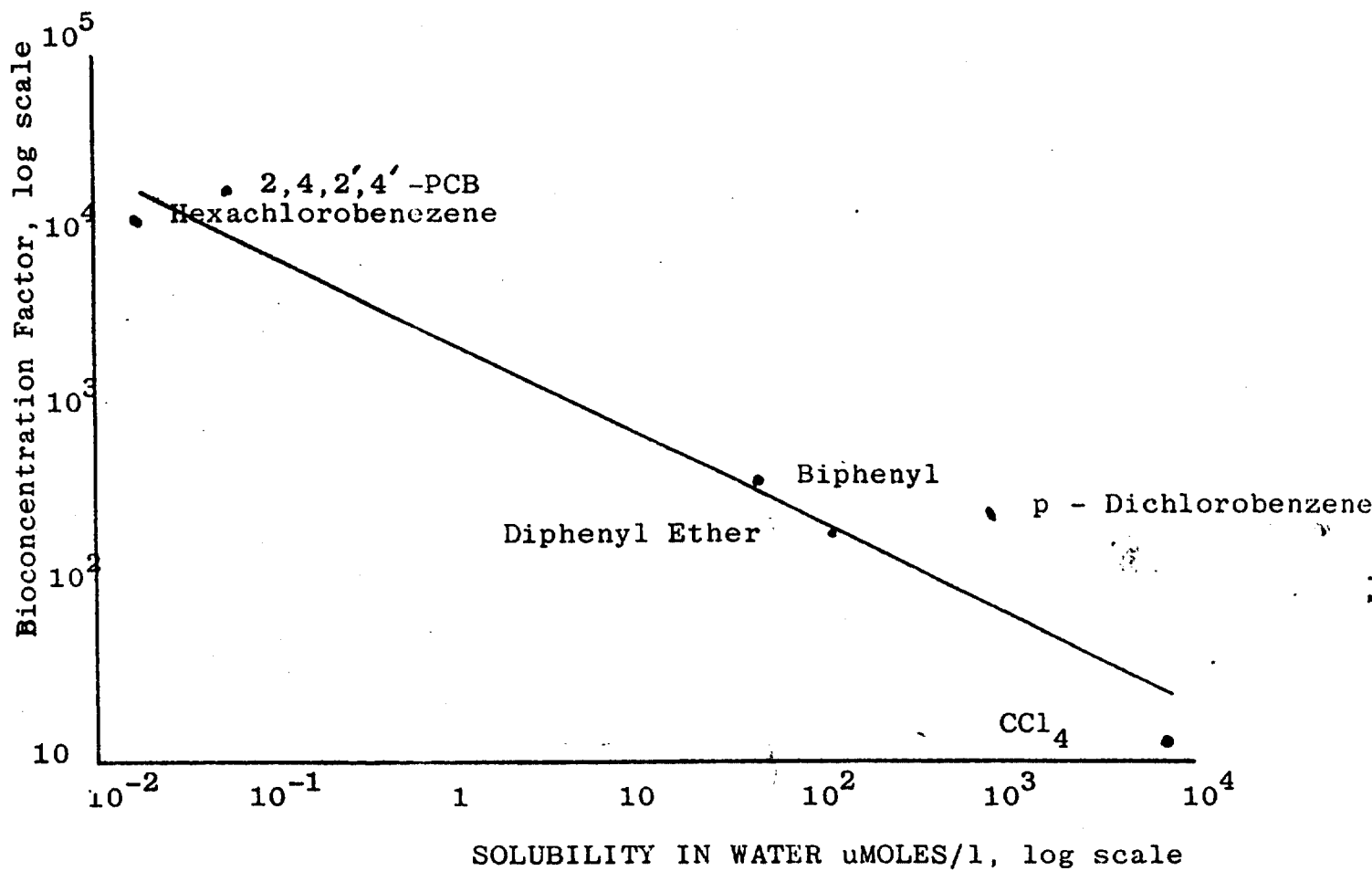
Figure 2
Relationship of Partition Coefficients to Water Solubility
of Organic Compounds



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Figure 3

Relationship of Bioconcentration Factor
to Water Solubility of Organic Compounds



EXPERIMENTAL

Volatility Studies on FM 3422

A. Rotary Evaporation under Reduced Pressure (41947-38, -39, -40)

Water, saturated with FM 3422 conducted in aquaria (see 42669-17), was used for samples, and a 5 ppm reference of FM 3422 in methanol was also prepared. GC analyses indicated the water thus saturated had a 5 ppm concentration of FM 3422 (note that this is high, based on the Veith technique used later. This high value may be due to supersaturation and/or micelle formation because these liquids had a large Tyndall effect, and the solutions were not filtered). A 25-ml water sample above was concentrated on a rotary evaporator under water aspirator pressure. The residue was taken up in octanol and gas chromatographed. Results showed that only 0.5 ppm of FM 3422 remained. A replicate experiment indicated that only 0.6 ppm of FM 3422 remained. Thus about ninety percent of this alcohol was lost due to volatilization.

B. Evaporation under Ambient Conditions (44191-43, -44; 46269-32)

A saturated aqueous solution of FM 3422 prepared and determined by the Veith technique (6; see 44191-43 and references therein) was shown to have a concentration of 0.05 ppm. For the evaporation study, 100 ml (vol. pipet) of this solution was transferred to a beaker and its contents allowed to evaporate (ca. 1.5 weeks). The beaker was rinsed with 2 ml (vol. pipet) of methanol, and an aliquot was gas chromatographed. Results indicated that 0.007 ppm of FM 3422 remained.

Reaction of FM 3422 with Alcoholic Potassium Hydroxide (48277-29, -31, -39; 46269-4, -5):

An alcoholic potassium hydroxide solution was prepared in a 500-ml round-bottomed flask (containing two joints, one a $\text{\textcircled{F}}$ 24/40 female and the other a $\text{\textcircled{F}}$ 10/30 female for aliquot withdrawal, and containing a teflon-coated magnetic stirrer bar, and an air-cooled condenser topped with an Ascarite^R protection tube) by dissolving 11.6 g of 86.2% potassium hydroxide (10 g if 100% KOH) in 200 ml of absolute alcohol. This solution was then maintained at 50-53° by an external oil bath for the duration of the experiment (504 hours).

One milliliter aliquots were withdrawn from this solution with a volumetric pipet through the normally closed $\text{\textcircled{F}}$ 10/30 entry port. This aliquot was quantitatively transferred to a 25-ml volumetric flask containing about 10 ml of absolute alcohol, one drop of phenolphthalein solution and three drops of concentrated nitric acid. The purpose was to stop any further reaction and to neutralize the base which proved to adversely affect the gas chromatographic

column used subsequently. The volumetric flask was diluted to the mark with absolute alcohol, and an aliquot of this solution was subjected to gas chromatographic analysis on the Hewlett-Packard Model 5813 gas chromatograph using electron capture detection.

To the above alcoholic KOH solution was added 40 mg of sublimed FM 3422, and immediately thereafter (solution of the FM 3422 required about 1 minute) a 1-ml aliquot was withdrawn and designated as time zero. Aliquots were removed and analyzed at times indicated in Table 1 and illustrated in Figure 4. A first-order reaction rate is shown by the following kinetic treatment (12):

$$\ln(a-x) = -kt + \ln a \quad \text{or}$$

$$\ln_{10}(a-x) = \frac{-k}{2.303} t + \ln_{10} a$$

Since for any experiment, a is a constant, the above is an equation for a straight line. When plotting $\ln(a-x)$ versus t , $\ln_{10} a$ will be the y intercept (found to be 2.2) with the slope equal to $-k/2.303$ and found to be -0.004.

Table 1
Alkaline Alcoholysis of FM 3422

<u>t (hrs.)</u>	<u>C (ppm)*</u>	<u>$\ln_{10} C$</u>
0	169	2.22
1	178	2.25
4	176	2.24
7	165	2.22
24	135	2.13
48	111	2.04
72	88	1.94
96	73	1.86
168	44.4	1.65
216	27.5	1.44
264	20.3	1.31
336	7.3	0.86
384	0.6	0.78
432	1.2	0.04
504	**	

* This number represents the average of two replicates done in duplicate.

** Poor electronic integration - no results:

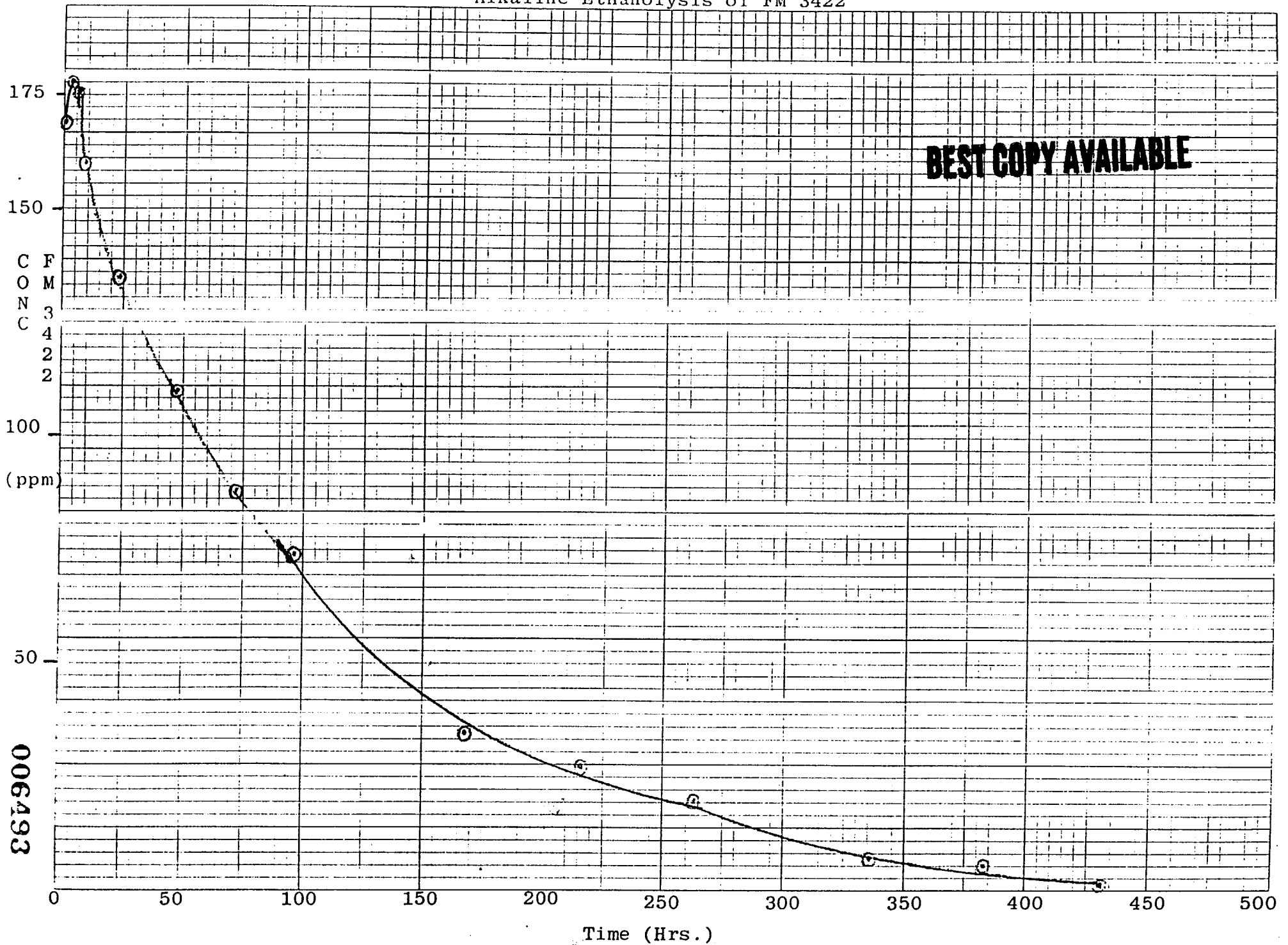
A plot of $\ln_{10} C$ versus time gives a slope of -0.004;

Since $k = -2.303$ (slope) then
 $k = -2.303 \times -0.004 = 9 \times 10^{-3} \text{ hr}^{-1}$

half life = $t_{1/2} = \frac{1}{k} \cdot \ln 2 = \frac{0.693}{9 \times 10^{-3}} = 77 \text{ hrs.}$

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Figure 4
Alkaline Ethanolysis of FM 3422



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FM 3422 Sorption onto Soil (46269-50)

Sorption-desorption soil studies were conducted by S. K. Welsh, and the results are given in Table 2.

Soil TLC (48277-30)

Various types of soil were ground and sieved, and that fraction of 262 micron size was saved for TLC studies (42669-42). An intimate mixture of 150 g of 262 micron size greenhouse soil (sandy loam) with 80 ml of water was well slurried and spread onto 10 x 20 cm glass plates using an in-house designed spreader (designed by J. W. Belisle, A. Mendel, and G. Guthrie). The plates were allowed to air dry. A plate was spotted 2 cm from the bottom with radiolabeled-FC-95, -FC-143, and -FM 3422. The samples were those used earlier for water solubility studies. The plate was air-dried and developed 100 mm from the original spot in the ascending mode with water in a filter paper-lined TLC developing tank previously equilibrated with water for one day. The development required nearly two hours and the air-dried plate was then autoradiographed (13). Results showed that FC-143 and FM 3422 did not leave the origin ($R_f=0$). The spot, due to FC-95, was extremely faint for visualization but appears not to have migrated either ($R_f=0$).

Preliminary Studies on Samples from Bionomics Labs

A. Examination of Foil-lined Caps for Interferences (46269-50)

Four foil-lined caps which Bionomics Labs uses to seal bottles containing samples were screwed onto four clean bottles containing 25 ml of deionized water. The bottles were mechanically shaken for 4 hours, and the combined 100 ml of water was extracted with ethyl acetate. This extract was concentrated and chromatographed. No apparent interference for FM 3422 was noted. This extract was then spiked with FM 3422 to confirm no interference at the retention time of FM 3422.

B. Examination of Standards and Controls Prepared at Bionomics Lab

Personnel from Bionomics Labs prepared standard solutions of FM 3422 in water, then submitted one-liter samples of these standards and controls to us for analyses. The respective sample was extracted with ethyl acetate and the organic extract was concentrated to 10 ml. An aliquot was used then for GC analyses, and the results are summarized in Table 3 (Notebook 46269-50).

Table 2

Sorption-Desorption Studies on FM 3422*

<u>Sample</u>	<u>Day</u>	<u>FM 3422 (ppm)</u>	<u>Day</u>	<u>FM 3422 (ppm)</u>	<u>Day</u>	<u>FM 3422 (ppm)</u>
32A	2/22/78	0.01	2/23/78	<0.002	2/24/78	0.002
32B	2/22/78	0.01	2/23/78	0.002	2/24/78	0.002
56A	2/22/78	0.01	2/23/78	0.003	2/24/78	<0.002
56B	2/22/78	0.22	2/23/78	0.005	2/24/78	<0.002
100A	2/22/78	0.22; 0.20	2/23/78	0.014; 0.019	2/24/78	<0.002
100B	2/22/78	0.19; 0.21	2/23/78	0.010; 0.011	2/24/78	<0.002
BKA	2/22/78	0.48; 0.51	2/23/78	0.044; 0.035	2/24/78	
BKB	2/22/78	0.49	2/23/78	0.029; 0.029	2/24/78	

*See interoffice memo of S. K. Welsh to D. L. Bacon,
FC Project, Soil Adsorption, Sept. 22, 1977 for methodology.

Table 3

Analyses for FM 3422 (in ppb) in Bionomics Samples

<u>Sample I.D.</u>	<u>Theoretical Conc. (ppb)</u>	<u>Determined</u>
A5609	20	20.8; 19.8
A5610	20	19.8; 20.6
A5611	10	10.2; 9.9
A5612	10	9.7; 10.1
A5613	5	5.2; 5.2
A5614	5	4.8; 5.1
A5615	2.5	2.5; 2.6
A5616	2.5	1.2; 1.3
A5617	1.25	(a)
A5618	1.25	(a)
A5619	Control A	<0.1
A5620	Control B	<0.1
A5621	Solvent Control A	<0.1
A5622	Solvent Control B	<0.1
A5670	1.25	1.1; 1.0(b)
A5670	1.25	1.0; 1.6(b)

(a) received broken in shipment; (b) replaces original samples A5617; A5618

006496

C. Examination of Water Samples for Possible Interferences of FC-143 (46269-53)

As done in Part B above, seven samples of water, received from Bionomics Labs were extracted with ethyl acetate, followed by diazomethane methylation and gas chromatography to determine if the water and the various containers holding samples may present interferences for the analysis of FC-143. All samples appeared to be free of interferences in the GC region for FC-143 analysis.

Studies on FC-95:

To Determine if FC-95 is Sorbed On/In Containers (47703-20, -22, -24)

Three 0.20-ml samples of ^{14}C FC-95 (aqueous solutions saturated by the Veith technique (42669-30)) were transferred to scintillation vials to which 15-ml Aquasol^R was added in each case. These control samples were labeled C-1, C-2, and C-3. Ten milliliters of the ^{14}C FC-95 saturated solution was transferred to each of the following containers: Polypropylene (PP), polyethylene (PE), polycarbonate (PC), and glass (G). Each container was tightly capped and allowed to stand at room temperature for one week, at which time the solutions were transferred to glass jars. The various containers were rinsed twice with 2-ml water and the rinses added to the respective jar. By pipet, 0.2 ml of the solution was transferred from the jar into a scintillation vial. This was repeated two times to generate three samples from each jar. Aquasol^R was added to each scintillation vial and then counted (13). These vials were labeled PP-1, PP-2, etc. Each of the saved containers from above was rinsed a first and a second time with 4 ml of methanol, and each rinse was transferred to a separate, clean vial. By pipet, 1 ml of the respective methanol rinse above was transferred to each of three scintillation vials containing Aquasol^R and then counted. The samples were labeled using the notation above, but the letter F for first rinse and S for the second rinse was added to the designation, e.g., PPF-1 indicates polypropylene container, first methanol rinse of the first sample, while GS-2 indicates a glass container, second methanol rinse of the second sample. The results are summarized in Table 4: Polypropylene was the first container of choice followed by polyethylene.

Studies on FC-143:

To Determine if FC-143 is Sorbed On/In Containers (47703-30, -37; 49400-51)

This experiment was performed essentially like that for FC-95, with the exception that the polycarbonate containers were not investigated. Various solvents attack polycarbonate (e.g., ethyl acetate). Control samples C-1, C-2, and C-3, as well as the 500-ppm ^{14}C FC-143 solution were transferred to polypropylene (PP)-, polyethylene (PE)-, and glass (G)-containers. Each container was tightly capped and allowed

Table 4

Sorption Studies on FC-95 (Labeled)

Part 1: Scintillation Counting on Samples

<u>Sample</u>	<u>dpm</u>	<u>Conc. mg/l FC-95</u>	<u>µg absolute</u>	<u>Avg. µg</u>
C-1	15,163	266	2660	2750
C-2	16,058	282	2820	
C-3	15,735	276	2760	
PP-1	11,294	198	2770	2730
PP-2	10,523	184	2580	
PP-3	11,585	203	2840	
PE-1	11,278	198	2770	2870
PE-2	11,808	207	2900	
PE-3	11,994	210	2940	
PC-1	11,493	201	2810	2790
PC-2	11,558	203	2840	
PC-3	11,138	195	2730	
G-1	11,840	208	2910	2850
G-2	11,252	197	2760	
G-3	11,760	206	2880	

Part 2: Scintillation Counting on Rinses

PPF-1	15.9	0.06	0.24	0.19
PPF-2	16.8	0.06	0.24	
PPF-3	7.22	0.02	0.08	
PPS-1	5.80	0.02	0.10	0.03
PPS-2	<Background	0.00	0.00	
PPS-3	<Background	0.00	0.00	
			Avg. Total	0.27
PEF-1	50.5	0.18	0.72	0.71
PEF-2	60.5	0.21	0.84	
PEF-3	40.5	0.14	0.56	
PES-1	26.1	0.09	0.45	0.37
PES-2	4.66	0.02	0.10	
PES-3	31.0	0.11	0.55	
			Avg. Total	1.08

Table 4 (continued)

<u>Sample</u>	<u>dpm</u>	<u>Conc. mg/l FC-95</u>	<u>µg absolute</u>	<u>Avg. µg</u>
PCF-1	1829	6.41	25.6	26.4
PCF-2	1865	6.54	26.2	
PCF-3	1958	6.86	27.4	
PCS-1	270.3	0.95	4.75	4.78
PCS-2	294.0	1.03	5.15	
PCS-3	254.0	0.89	4.45	
Avg. Total				31.18
GF-1	140.9	0.49	1.96	1.99
GF-2	140.6	0.49	1.96	
GF-3	146.1	0.51	2.04	
GS-1	126.8	0.44	2.20	2.17
GS-2	118.6	0.42	2.10	
GS-3	125.5	0.44	2.20	
Avg. Total				4.16

to stand at room temperature for one week, at which time the solutions were transferred to glass jars. The various containers were rinsed twice with 2 ml of water and the rinses added to the respective jar. By pipet, 0.2 ml of the solution was transferred from the jar into a scintillation vial. This was repeated two times to generate three samples from each jar. Aquasol^R was added to each vial and then counted. These vials were labeled PP-1, PP-2, etc. Each of the saved containers from above was rinsed a first and a second time with 4-ml methanol, and each rinse was transferred to a separate, clean vial (in the case for the glass container, 3 ml rather than 1 ml of methanol was used for the first transfer, thus GF-2 contained 1 ml of rinse and GF-3 had to be eliminated). By pipet, 1 ml of the respective methanol rinse above was transferred to each of three scintillation vials containing Aquasol^R and then counted. The samples were labeled with the notation mentioned earlier. The results are given in Table 5. Polypropylene, the container of choice, was used in subsequent experiments.

Solubility of FC-95 in Water (47703-15)

The Veith technique (6) for saturating water with organics was conducted using radiolabeled FC-95 as described in Notebooks 287103-5 and 42669-30. Three 0.25-ml samples were withdrawn from the saturator at 0, 1, 2, 4, 6, 24, and 48 hours. The samples were placed in scintillation vials to which 15 ml of Aquasol^R was added, and counts were taken on the Nuclear Chicago scintillation counter (Agrichem). The solubility results are tabulated below:

<u>Hr.</u>	<u>mg/l FC-95</u>
0	0
1	226
2	238
4	282
6	280
24	292
48	291

Avg. (Hrs. 4-48) = 286

Quantitation of FC-95 by the Methylene Blue Method (47703-44)

FC-95 was quantitated by the methylene blue method for methylene blue-active substances as detailed in Standard Methods for the Examination of Water and Wastewater (10). Known concentrations of FC-95 (100 ml, see below) were added to each of five separatory funnels followed by 25 ml of methylene blue reagent and 10 ml of chloroform. The funnels were shaken for one-half minute and the contents were allowed to separate. The desired organic phase was withdrawn through glass wool and collected. The percent transmission of the organic phase was determined after the Spectronic 20 instrument was first calibrated (652 nm) with chloroform. The concentration versus percent transmission is shown in Table 6 and illustrated in Figure 1.

Table 5

Sorption Studies on FC-143 (Labeled)

Part 1: Scintillation Counting on Samples

<u>Sample</u>	<u>dpm</u>	<u>Conc. mg/l FC-143</u>	<u>µg absolute</u>	<u>Avg. µg</u>
C-1	34,456	534	5340	5350
C-2	34,521	535	5350	
C-3	34,599	536	5360	
PP-1	24,829	385	5390	5325
PP-2	24,560	381	5334	
PP-3	24,190	375	5250	
PE-1	23,664	367	5138	5143
PE-2	24,078	373	5222	
PE-3	23,409	362	5068	
G-1	24,962	387	5418	5465
G-2	25,546	396	5544	
G-3	25,002	388	5432	

Part 2: Scintillation Counting on Rinses

PPF-1	293	0.91	3.6	3.6
PPF-2	270	0.84	3.4	
PPF-3	296	0.92	3.7	
PPS-1	21.5	0.07	0.35	0.35
PPS-2	20.9	0.06	0.30	
PPS-3	25.3	0.08	0.40	
Avg. Total				3.95
PEF-1	16,936	52.5	210	213
PEF-2	17,268	53.5	214	
PEF-3	17,430	54.0	216	
PES-1	859	2.7	13.5	13.0
PES-2	849	2.6	13.0	
PES-3	802	2.5	12.5	
Avg. Total				226
GF-1	13,530	14.0	56.0	55.4
GF-2	4,414	13.7	54.8	
GS-1	124	0.38	1.9	1.0
GS-2	129	0.40	2.0	
GS-3	126	0.39	2.0	
Avg. Total				57.4

006501

Table 6

FC-95 by Methylene Blue

<u>Concentration of FC-95</u> (ppm)	<u>% Transmission</u>
0.0	100
0.06	76
0.12	56
0.20	40
0.40	17

Note that FC-95 can be quantitated in this range; however, the limitations are that any methylene blue-active substances such as anionic surfactants or other sulfonic acids will present a positive interference.

GC Calibration and Recovery Studies on FC-143 (46269-34, -54)

The purpose of this work was to prepare absolute standards of FC-143 and to evaluate recovery from water. An internal standard of perfluorodecanoic acid (obtained from Dr. Jon Belisle, CRL) was prepared by weighing and dissolving 0.100 g of this acid into 100 ml of hexane (1000 ppm). A standard of 1000 ppm of FC-143 (lot 83) was made by weighing and dissolving 0.100 g of FC-143 in 100 ml of methanol. For acidification of aqueous solutions, 1 g of p-toluene sulfonic acid (PTSA) in 100 ml of methanol (10^4 ppm) was prepared, and 2-3 drops of this solution was added to extractants prior to diazomethane methylation. Samples prepared for GC was as follows: In a 20-ml vial was placed 5 ml benzene and in a second vial was placed 5 ml of 10% ether in hexane. Each vial was spiked with 20 μ g of the FC-143 and with 20 μ l of the internal standard. Three drops of PTSA were added to each vial followed by ethereal diazomethane. After 15 minutes of reaction time, excess diazomethane was removed (N_2 purge) and the samples were diluted to 10 ml (volumetric flask) followed by GC. Results showed that benzene was superior to ether-hexane as a solvent (larger integrator response). Furthermore, the electron capture response to FC-143 (as the methyl ester) was different from that to the perfluorodecanoic acid (as the methyl ester). Accordingly, various concentrations of both these acids were made, followed by methylation and gas chromatography. An average response factor was thus obtained. Then, 0.1 and 1 ppm standards of FC-143 were prepared in water. The water sample, containing the internal standard acid, was benzene extracted, concentrated, acidified (PTSA), and methylated in the usual manner. GC of the samples showed recoveries of 93% and 100.4% for the 0.1 ppm solution and 90.9% and 99.4% for the 1 ppm solution.

TLC OF Biodegradation Studies on Radioactive FC-95, FC-143, and FM 3422 (47703; 6-14, 21, 25-27, -35; 39-43, 46)

Details of the biodegradation studies on labeled FC-95, FC-143, FM 3422, and controls are described in E. A. Reiner's report (14). In the present work, the nineteen samples each from sludge, water, and ethyl acetate extracts generated from biodegradation studies were applied directly to plates (20x20 cm, E. Merck GF 254 silica gel). The plates were developed in ethyl acetate then examined first by ultraviolet light (long and short wavelength) and then by autoradiography. The plates were exposed to Kodak x-ray film for one week, and the film was then developed and examined. Comparison with control samples indicated no significant differences.

In a second part of this experiment, a portion of the ethyl acetate extract from the various samples was methylated with diazomethane to convert any nonvolatile components to GC volatile species. Both the unmethylated and methylated samples were then analyzed by gas chromatography. No differences were noted between these and control samples. GC conditions are detailed in Notebook 47703-43.

Determination of the Solubility of N-Methyl FOSE Alcohol FM 3925 (48277-8; 46269-53; 42669-4)

About 20 g of FM 3925 Lot 505 was melted (steam bath) to obtain a homogeneous sample. The cooled, solid material, 200 mg, was dissolved in about 200 ml of reagent grade acetone, and this solution was added to precleaned 2 mm diameter solid glass beads contained in a beaker. Beads were precleaned successively with heptane, chloroform, acetone, water, methanol, and then air dried. The FM 3925 coated glass beads were placed in a glass column (350x18 mm) and supported by glass wool (pretreated with Glastreat^R). The end rubber stoppers were connected to Bev-Line V^R tubing and a peristaltic pump was used to circulate deionized water through the column. The entire setup was conducted in the dark in a temperature-controlled walk-in environmental room (18±1°). Prior to the start of this experiment, water was pumped for 5 hours through the setup, and this water was discarded. The purpose of this was to remove any impurities that would be as soluble as, or more soluble than, FM 3925. Fresh water was then placed into the system and at intervals (see Table 3), 100 ml (volumetric pipet) of water was withdrawn from the main 2-liter storage chamber. Each of the 100 ml samples was quantitatively transferred to a separatory funnel, and 10 ml of saturated aqueous sodium chloride was added followed by 15 ml of ethyl acetate. The mixture was extracted and the separated organic phase was quantitatively transferred to a 10-ml volumetric flask. The aqueous phase was reextracted with 4 ml of ethyl acetate, and the organic phase was added to the 10-ml volumetric flask whose volume was finally brought to the mark with ethyl acetate. An aliquot was used for gas chromatography using an electron capture detector and a six-foot (1.8 meters) column of Carbowax CW20M run at 180°. The results are reported in Table 3.

Table 3
Solubility of FM 3925 in Water

<u>Time of Water Circulation (hrs.)</u>	<u>FM 3925 (ppm)</u>
1	1.72; 1.82
2	1.90; 1.87
4	2.10; 2.17
6	2.33; 2.30
8	2.34; 2.35
24	2.17; 2.14

Avg. (Hrs. 4-24) = 2.3 ppm

The solubility of FM 3925 is forty-six times that of FM 3422. The retention time of FM 3925 is close to that of FM 3422, and the gas chromatographic patterns (see Figure 2 in reference 1) are essentially the same.

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