BIOACCUMULATION

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.

METHOD:

Method/guideline followed: None given for sampling of the organisms. Extraction and analysis procedures were devised by 3M.
Type: Analysis of tissue for fluorochemical from indigenous fish caught in the Tennessee River above and below the Wheeler Dam.
GLP (Y/N): No
Year: 1979

Remarks field: There is no information on sampling procedures of the organisms from the Tennessee River near the manufacturing facility.

Four fish were caught and utilized as samples; Two channel catfish caught above Wheeler Dam, one white bass caught below and one white crappie caught above Wheeler Dam. Wheeler Dam is approximately 26 nautical miles downstream from the 3M Decatur Plant effluent discharge. It was not noted in the report how many miles above and below the dam the fish were caught.

A ten ppm standard of FM-3422 (N-EtFOSE alcohol) was prepared by diluting 1 ml of a 100 ppm standard (in ethyl acetate) to mark with ethyl acetate in a 10 ml volumetric flask.

One whole channel catfish was homogenized to create one sample. The other channel catfish was dissected and the various individual parts were homogenized to create individual samples.

The white bass had a 6.3 cm i.d. dinker die core sample taken just off the lateral line behind the gill plate making up a 20.591 g sample containing skin, filet, small part of the backbone, reproductive organs, part of the kidney, and rectum.

The white crappie had a dinker die core sample taken behind the gill plate to create a 16.684 gram sample containing filet, vertebrae, skin and bile.

All samples were homogenized in known volumes of DI water and divided into five aliquots each.

Samples were centrifuged, extracted with ethyl acetate, and analyzed by GC for organic and inorganic fluoride.

It was noted that FM-3925 (N-MeFOSE alcohol) and FM-3422 (N-EtFOSE alcohol) could not be distinguished with GC with electron capture parameters. The results are therefore a combined value.

RESULTS

N-MeFOSE alcohol / N-EtFOSE alcohol Concentration
In Tennessee River Fish by GC

Sample	N-MeFOSE alcohol & N-EtFOSE alcohol (ppm)
Water blank	N.D.
Ethyl Acetate blank	N.D.
Whole Channel Catfish	0.73
White Bass core sample	3.31
White Crappie core sample	N.D.
Channel Catfish Gills	0.80
Channel Catfish Liver	0.38
Channel Catfish Parts*	0.43
Channel Catfish Muscle	N.D.
Channel Catfish Fat **	6.12
Channel Catfish Gall Bladder	0.74

Upon completion of GC analysis, there was concern that the values were not definitive. Additional analysis of ethyl acetate homogenate extract was then done using Capillary Gas Chromatography with Electron Capture and GC using a Microwave Sustained Helium Plasma Detector.

Qualitative analysis of the fish extracts using Capillary Gas Chromatography with electron capture failed to identify the presence of N-EtFOSE alcohol. This was further supported by analysis by a Microwave Sustained Helium Plasma Detector where again, no evidence of any fluorochemicals were detected and specifically no N-EtFOSE alcohol and no N-EtFOSA (F-6309) were detected. The results obtained by the microwave plasma detector on spiked samples indicated that N-EtFOSE alcohol, if present, could have been detected from its fluorine content at 0.1 ppm in the ethyl acetate extracts. No reference was made to N-MeFOSE alcohol except for the general statement made "No fluorocarbon peaks were observed in the actual samples."

Remarks: The original report (5/22/79) referenced a sample for FM-3923. It was brought up after the report was generated that FM-3923 and FM-3422 are both the same coumpound (N-EtFOSE alcohol). Analytical was conducted to verify its

identity and it was found to be N-EtFOSA (F-6309). The attached report ("AR No. 7238 – Determination of Fluorinated Alcohols in Fish Extracts", 10/23/79) still refers to FM-3923 when in fact the sample labeled as FM-3923 is F-6309. This report also has inconsistencies. The last paragraph indicates the ability to detect fluorine content at 0.1 ppm level. However, a review of the procedure used indicates a detection limit of 0.5 ppm.

The first report (5/22/79) describes analysis of ethyl acetate extracts of fish homogenate by gas chromatography (GC) with electron capture detection. The analysis shows the presence of materials in fish tissue extracts that have GC retention times identical to both N-MeFOSE alcohol and N-EtFOSE alcohol and to N-EtFOSA. The GC retention times of N-MeFOSE alcohol and N-EtFOSE alcohol standards were the same (not resolved) by the method used in the first report. The first report indicates the presence of fluorochemicals in the fish extracts, but electron capture detection is not specific for fluorochemicals. Thus the results reported in the first report were not a specific identification of fluorochemicals detectable by GC. (Report 1 also has errors in column 4 of Table 1. In the 1B row, 0.40 should be changed to 4.13, and in the 2A row, 0.004 should be changed to 0.06.)

The second report (12/28/79) shows a misinterpretation in the first report. It includes a description of GC analyses of ethyl acetate extracts of two of the samples described in report 1 samples 1B and 3A. The work described in report 2 used electron capture detection and references a report using microwave sustained helium plasma detection (MSHPD) in the fluorine and sulfur mode. In fluorine mode, MSHPD method is specific for fluorine. The MSHPD results show no fluorochemicals in the ethyl acetate extracts. The results are interpreted as indicating that F-6309 and N-EtFOSE alcohol (FM-3422) are present in the ethyl acetate extracts at less than 0.1 ppm. In the first report, N-EtFOSA (F-6309) and N-MeFOSE alcohol (FM-3925) / N-EtFOSE alcohol (FM-3422) had appeared to be present respectively at 0.82 and 3.31 ppm in sample 1B and at 1.48 and 0.80 ppm in sample 3A. Thus, the GC-able compounds seen in the first report appear not to have been fluorochemicals and thus could not have been N-MeFOSE alcohol, N-EtFOSE alcohol or N-EtFOSA.

The first report shows the presence of unidentified organic fluorine and of inorganic fluorine in the fish tissue. This was not re-evaluated in the second report.

CONCLUSIONS

No reliable conclusions can be derived from this study.

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

DATA QUALITY

Reliability: Klimisch ranking 3. Without an understanding of the sampling design in relation to the outfall and sampling points, verifiable data on the actual concentrations of fluorochemicals in the river from both the manufacturing facility and from natural sources, activities in the manufacturing facility prior to sampling, any applicable environmental conditions (e.g. rain events), and a clear understanding of how long the sampled fish were in the sampling area, there is little to be concluded. Additionally, the analytical data conflicts. It cannot be definitively concluded which analytical data set is correct. Extraction and analytical methodology were not validated. State units of results is ppm. It is not correlated to mg analyte per kg body weight. Identity and purity of reference compounds was not established therefore stated analyte concentrations have no basis in fact.

REFERENCES

3M Technical Report "Bioaccumulation of Fluorochemicals in Tenn. River Fish." James E. Gagnon, Project 78-2740, Decatur, Alabama – Tennessee River Fish, Report Number 001, May 22, 1979

3M Technical Report "AR No. 7238 – Determination of Fluorinated Alcohols in Fish Extracts." D. F. Hagen, Project A000007, Environmental Engineering and Pollution Control, Report Number 238, October 23, 1979.

3M Technical Report "Fluorochemicals in Tennessee River Fish." James E. Gagnon, Project 78-2740, Decatur, Alabama – Tennessee River Fish, Report Number 100, December 28, 1979

3M requested expert overview, "Bioaccumulation Studies", Dr. James Gillett, Cornell University, March 8, 1993

OTHER

Last changed: 5/18/00

3M
Form 6747-11-A

TECHNICAL REPORT SUMMARY

Date: 5/22/79

TO: TECHNICAL COMMUNICATIONS CENTER – 201-2CN

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

DEC 20 1979

Division: Environmental Laboratory (EE & PC)	Dept. Number: 0222
Project: Decatur, Alabama - Tennessee River Fish	Project Number: 78-2740
Report Title: Bioaccumulation of Fluorochemicals in Tenn. River Fish	Report Number: 001
To: D. L. Bacon	
Author(s): James E. Gagnon	Employee Number(s): 213531
Notebook Reference: 51568 Lab Request #4871	No. of Pages Including Cover Sheet: 10 (2)

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
Decatur

CURRENT OBJECTIVE: Qualitative and quantitative determination of F 6309, FM-3925, and FM-3422 in fish taken from the Tennessee River above and below Wheeler Dam at 3M's Decatur plant. Analyze for organic and inorganic fluoride in the same samples.

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.

Ethyl acetate extracts of a Channel catfish (Ictalurus punctatus), white bass (Roccus chrysops), and a white crappie (Pomoxis annularis) were analyzed by gas chromatography.

cc: D. Ricker-236-2B
A. Welter
A. Mendel

Information Liaison Initials: ERL

INTRODUCTION

It is known that 3M's Decatur, Alabama plant effluent has high organic fluoride levels, 10.9 ppm (1)(2). It has also been shown that fluorochemicals can bioaccumulate in fish in a laboratory environment (3)(4). With these combined factors, the next step was to see if fish caught in the Tennessee River near the Decatur plant had detectable levels of fluorochemicals.

RESULTS AND DISCUSSION

Table 1 lists the concentration, in ppm, in fish of compounds which have the same retention time as the three fluorochemicals of interest (F-6309, FM-3925, and FM-3422).

Analysis of the results for the dissected channel catfish, Sample 3A, shows that the fluorochemicals bioconcentrate to a greater extent in the gastrointestinal tract, reproductive system, and fat. It can also be seen that the muscle layer was found not to bioaccumulate the three fluorochemicals of interest. These results agree with earlier reports (3)(4).

When comparing the total fluorochemical content (TFC) for the two whole fish samples, the larger channel catfish contained more than twice the fluorochemical content, 2.74 ppm vs. 1.13 ppm. Since both fish were caught in the same area, a reasonable explanation for this may be related to the high partition coefficients for channel catfish. Fluorochemicals bioaccumulate in fatty tissue, and since more fatty tissue is present in the larger fish, more fluorochemicals would be expected.

F-6309 is present at higher concentrations in the dissected channel catfish, sample 3A, than other samples. Since bioaccumulation rates have not been determined for F-6309 no explanations for the higher concentrations can be offered.

The two fish samples which had cores taken from them will not be rigorously compared to whole fish samples. The reason for this is that the core samples may not have representative concentrations of fluorochemicals (whole fish values may be higher or lower). Since core samples were taken from the approximate same location, the results can be rigorously compared.

The white bass from below Wheeler Dam, sample 1B, had a whole fish TFC of 0.40 ppm, while the white crappie from above Wheeler Dam, sample 2A, had a whole fish TFC of 0.004 ppm. With such small statistical samples, it would be difficult to say that the larger TFC is due only to the white bass living in the presence of higher fluorochemical concentration, downstream from the plant. Other possible explanations for the higher TFC could be the following:

TABLE 1

FLUOROCHEMICAL CONCENTRATION (ppm)
IN TENNESSEE RIVER FISH

Sample	F-6309	FM-3925 & FM-3422 (1)	Total Combined FC in Fish (ppm) (2)
1A - Whole fish	0.40	0.73	1.13
1B - Core (3)	0.82	3.31	0.40 (4)
2A - Core (5)	0.06	N.D. (6)	0.004 (4)
3A - Gills	1.48	0.80	
3A - Liver	2.17	0.38	
3A - Parts (7)	1.33	0.43	2.74 (9)
3A - Muscle	N.D.	N.D.	
3A - Fat (8)	13.85	6.12	
3A - Gall bladder	1.57	0.74	
Water blank	N.D.	N.D.	
Ethyl acetate blank	N.D.	N.D.	

Footnotes to Table 1:

(1) FM-3925 and FM-3422 cannot be resolved with GC parameters used; therefore, a combined value is reported.
(2) Based on frozen weight of the fish.
(3) Sample core, 3.61 cm, id contained skin, filet, reproductive organs, and parts of kidney, rectum, and backbone.
(4) Assumes that the concentrations obtained in the core are representative of the rest of the fish.
(5) Sample core, 3.61 cm id contained filet, vertebrae, skin, and bile.
(6) N.D. = Not detected.
(7) Consisted of muscle, skin, blood, bone, and cartilage.
(8) Consisted of gastrointestinal tract, reproductive system, and fat.
(9) Based on the actual weight of sample used, 18.8% less than frozen weight, and weight percent of each part.

1. Longer river residence time, older fish.
2. Longer location residence time.
3. Different species
   a) Different feeding and life styles
   b) Contains larger weight percent of organs which tend to bioaccumulate fluorochemicals
   c) Larger fluorochemical partition coefficients

If the core samples are representative of whole fish concentrations, then it can be postulated that channel catfish bioaccumulate fluorochemicals to a greater extent than either white bass or crappie. Reasons for this are the same as listed above.

Table 2 gives the results of the organic (RF) and inorganic fluoride (F^{Θ}) concentration, in ppm, in the fish samples.

TABLE 2 (5)

ORGANIC (RF) AND INORGANIC (F^{Θ}) FLUORIDE CONCENTRATIONS (ppm)

Sample	RF	F^{Θ}
1A	9.7	24.6
2A	16.2	13.3
1B	10.5	6.2
Water	N.I.	0.01

Jon Belisle points out that the high inorganic fluoride values seem rather surprising. His only explanation was that fish flour previously analyzed, for a different requestor, was shown to have inorganic fluoride values higher than organic fluoride. Jon also states that high inorganic fluoride values would make it difficult to calculate low levels of organic fluoride.

Comparison of the organic and inorganic fluoride content shows that samples from above Wheeler Dam have just as high, if not higher, values than for the sample from below the dam. There are no clear cut explanations for this observation. An earlier analysis of Tennessee River water showed high organic fluoride concentrations upstream from the plant. At that time, it was thought the samples may have been mislabeled. With these results,

Steve Welsh
2/12/80

it would seem to indicate that the concentration of fluorochemicals may actually be less below Wheeler Dam. This may be caused by volatilization of the fluorochemical when going over the dam (1), settling of fluorochemicals before the dam.

Comparison of organic fluoride values from Tables 1 and 2 show no correlation. For example, the highest organic fluoride value, 16.2 ppm for sample 2A, had the lowest TFC, 0.004 ppm, for the fluorochemicals analyzed. A possible explanation is that there are organic fluorides present in very high concentrations which were not analyzed for individually. The species which had the highest fat content, channel catfish, had the lowest organic fluoride concentrations.

With limited sample population (2 fish of one species and one of each of two other species), it is difficult to draw any meaningful conclusions. The only definite conclusion is that the fluorochemicals studied do appear to bioaccumulate in river fish under natural conditions.

EXPERIMENTAL

1. Sample materials

Fish

1A - Small channel catfish *(Ictalurus punctatus)*, caught above Wheeler Dam in Tennessee River.

1B - White bass *(Roccus chrysops)*, caught below Wheeler Dam in Tennessee River.

2A - White crappie *(Pomoxis annularis)*, caught above Wheeler Dam in Tennessee River.

3A - Large channel catfish *(Ictalurus punctatus)*, caught above Wheeler Dam in Tennessee River.

Standards

FC-6309, FM-3925, and FM-3422.

Ten ppm standards of FC-6309, FM-3925, and FM-3422 were prepared by diluting 1 ml of a 100 ppm standard, in ethyl acetate, to mark with ethyl acetate in separate 10 ml volumetric flasks.

2. Analysis Instruments/Materials

Blender:

Waring Commercial blender, Model #91-263, available from Waring Products Division, Route 44, New Hartford, CT 06057.

following:

Tissuemizer:

Model #SDT, available from Tekmar Company, P. O. Box 37202, Cincinnati, OH 45222.

Dinker Die:

3.61 cm id AISI-02 high carbon steel cutting die made by Jerry Guthrie in Central Research Labs, described in 3M Technical Notebook #51568-35.

Mixer:

"Vortex Genie" Model #K-550-G, available from Scientific Industries, Inc., Bohemia, NY 11716.

Centrifuge:

Damon-IEC Model #B-20A, available from Damon-IEC Corporation, Needham Heights, MA.

Bottles:

Four-ounce widemouthed clear glass bottle sealed with aluminum foil and aluminum foil-lined caps.

125-ml linear polyethylene (LPE) plastic bottle with polyseal caps.

Gas Chromatograph:

Chromatograph - Hewlett-Packard Model 5713 GC.
Integrator - Hewlett-Packard Model 3380A integrator-printor.

Both of the above available from Hewlett-Packard Co., 150 Page Mill Road, Palo Alto, CA 94304.

Column - Six-foot, 1/8 inch OD, stainless steel, packed with 10% CW20M on 60/80 Chromasorb W-AW.

Column Temperature - Isothermal 180° C.
Injector - On-column at 200° C.
Detector - Electron Capture at 300° C.
Flow - ~40 cc/minute of Argon:Methane (95/5).

Ethyl Acetate:

"Li Chrosolv" chromatography solvent available from MC/B Manufacturing Chemists, 2909 Highland Avenue, Norwood, OH 45212, as Catalog #6008688M.

and fat.
(9) Based on the actual weight of sample used, 18.8% less than frozen weight, and weight percent of each part.

Water:

Deionized water.

3. Procedure (6)

Procedures used below, except for minor modifications, were obtained from earlier 3M Technical Report summaries (7).

Samples 1A through 3A and 1B were removed from the freezer and placed in large aluminum pans, in a fume hood, and allowed to thaw.

A whole channel catfish, sample 1A, was cut into 5 sections and homogenized in a blender with 200 ml water.

Sample 1B had a dinker die core sample taken just off the lateral line behind the gill plate. Contents of the 20.591 gram sample were skin, filet, small part of backbone, reproductive organs, part of kidney, and rectum.

Sample 2A had a dinker die core sample taken behind the gill plate. The 16.684 gram sample contained filet, vertebrae, skin, and bile. Samples 1B and 2A were homogenized with 10 ml of water in a "tissuemizer."

Sample 3A was dissected, and the various individual parts were homogenized with water. Individual parts weighing more than 25.0 grams were homogenized in a blender, while those of lesser weight were homogenized in a "tissuemizer." Table 3 lists the sample, sample weight, and amount of water added for homogenizing each sample.

All of the above samples, after homogenization, were divided into five aliquots and placed in precleaned bottles, (dichromate/acid, water rinse, dry, toluene, dry). Three aliquots were placed in LPE bottles, while the other two were placed in glass bottles. Samples were stored in a refrigerator at 4.5° C. until needed.

Samples analyzed for F-6309, FM-3925, and FM-3422 were prepared according to the following procedure. See Table 4 for weight of sample and milliliters of ethyl acetate used for extractions.

A previously homogenized sample, stored in a glass bottle, was weighed (no larger than 4.00 g) and added to a 30-ml precleaned glass centrifuge tube. A volume of ethyl acetate was added at the rate of 1.0 ml ethyl acetate per gram of homogenate. The ethyl acetate/fish homogenate were mixed for 1.5 minutes in a mixer at a speed setting of 3. The samples were removed and centrifuged at 1500 rpm at

21° C. for 10 minutes. After centrifuging, the ethyl acetate layer was separated, by use of a pipet, and placed in a vial. Five µl of sample (standard) was injected for gas chromatographic analysis.

Samples 1A, 2A, and 1B homogenates, plus a water blank, in LPE bottles, were sent to Jon Belisle of the Central Research Laboratory for organic and inorganic fluoride analysis.

REFERENCES

(1) 3M Technical Report Summary, August 30, 1978, Arthur Mendel to R. L. Bohon, "Fate of Fluorochemicals Project - Progress Report."

(2) Central Research Laboratory Report Number 6902, April 20, 1978, Jon Belisle.

(3) "Bioconcentration of FM-3422 in Bluegill Sunfish and in Channel Catfish," M. T. Elnabarawy to A. N. Welter, May 17, 1977.

(4) 3M TRS, August 16, 1978, A N. Welter to D. L. Bacon, "Evaluation of the Bioconcentration Potential of FM-3422."

(5) Central Research Laboratory Report on Request #A72199 by Jon Belisle, May 7, 1979.

(6) Experimental work done in cooperation with A. N. Welter of the Environmental Laboratory (EE & PC), who performed the dissections and homogenizations.

(7) 3M Technical Report Summary, November 15, 1977, A. Mendel to D. L. Bacon, "Analytical Methodology on FM-3422."

James E Seguin

JEG/cen

TABLE 3

FISH WEIGHTS AND WATER VOLUMES USED FOR HOMOGENIZATION

Sample Description	Initial Whole Frozen Weight	Actual Sample Weight Used	ml Water Used
1A	146.0 g	Whole fish (1)(2)	200
2A	266.5 g	16.684 g (3)	10
1B	210.0 g	20.591 g (3)	10
3A - Muscle	752.0 g	209.93 g	200
3A - Gall bladder	752.0 g	1.378 g	10
3A - Liver	752.0 g	5.949 g	10
3A - Fat	752.0 g	52.230 g	100
3A - Parts	752.0 g	321.57 g	300
3A - Gills	752.0 g	19.38 g	100

Footnotes:

(1) A fish hook, with no apparent rust or line, was found in fish and was removed before homogenization.

(2) The fish appeared to be slightly dehydrated (possibly due to constant air flow over surface of fish) so the actual weight of fish used may have been less than frozen weight.

(3) Sample core 3.61 cm id.

TABLE 4

FISH WEIGHTS AND ETHYL ACETATE VOLUMES
USED FOR EXTRACTIONS

Sample Description	Weight of Fish Homogenate (grams)	% Water in Homogenate	Actual Fish Wt. Extracted (mg)	ml EtOAc
3A - Gall Bladder	1.20	87.9	145.2	1.2
3A - Liver	2.20	62.7	820.6	2.2
3A - Muscle	2.40	48.8	1228.8	2.4
3A - Fat	2.40	65.7	823.2	2.4
3A - Parts	3.00	48.3	1551.0	3.0
3A - Gills	3.00	83.8	486.0	3.0
Water Blank	2.40	100.0	--	2.4
1A	2.40	57.8	1012.8	2.4
1B	2.40	32.7	1615.2	2.4
2A	2.40	37.5	1500.0	2.4

File Fate of FC — File Correspondence file (CC)

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Form 6747 11 A

TECHNICAL REPORT SUMMARY

Date 12/28/79

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: 0222
Project: Decatur, Alabama - Tennessee River Fish	Project Number: 78-2740
Report Title: Fluorochemicals in Tennessee River Fish	Report Number: 100
To: D. L. Bacon	
Author(s): James E. Gagnon	Employee Number(s): 213531
Notebook Reference: 51568 Lab Request #4871	No. of Pages Including Coversheet: 3

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
Decatur

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.

The microwave sustained helium plasma detector system and capillary column with electron capture were utilized to examine fish extracts for fluorocarbon alcohol levels.

cc: D.Ricker-53-4
A.Welter
A.Mendel

Information Liaison Initials SKle

Introduction:

Previous work[1] indicated a need for more definitive answers to the presence of volatile fluorochemicals. Capillary gas chromatography with an electron capture detector (CGCEC) and microwave sustained helium plasma detector (MSHPD) were used to analyze ethyl acetate extracts of fish taken from the Tennessee River, near 3M's Decatur, Alabama plant. A Minnesota brown bullhead sample, extracted as previously described[1], was also analyzed as a background check.

Results:

1. Capillary Gas Chromatography with Electron Capture

No compounds were detected in the Minnesota brown bullhead (sample 1M) having retention times close to the fluorochemical standards (Table 1). Except for a peak at 6.14 minutes, and solvent peaks, the chromatogram was very clean. In comparison, samples 1B and 3A (bass and catfish from below and above Wheeler Dam, respectively) showed more than 25 peaks. A peak with retention time similar to F-6309 was detected in samples 1B and 3A (Table 1).

TABLE 1

QUALITATIVE ANALYSIS OF FISH EXTRACTS FOR FLUOROCHEMICALS

Sample	Retention Time (Minutes) 10.84	12.68
1B	**	N.D.
1M	N.D.	N.D.
3A	*	N.D.
FM-3422 Std.	N.D.	***
F-6309 Std.	***	N.D.

N.D. = Not detected
* = Very small amount
** = Peak Area less than standard, but greater than *
*** = 10 ppm standard

2. Microwave Sustained Helium Plasma Detector: (MSHPD)

The above samples were also analyzed by MSHPD in the fluorine and sulfur detection modes. The results obtained by the microwave plasma detector on spiked samples show that FM-3422 and F-6309, if present, could have been detected from their fluorine content at the 0.1 ppm level in the ethyl acetate extracts. No fluorocarbon peaks were observed in the actual samples.[2]

Discussion:

The above results indicate that no volatile fluorocarbons were present in samples. The large amounts of organic fluorine mentioned in the original report[1] are due to the presence of nonvolatile fluorochemicals (NVFC). Thin-layer chromatography for NVFC's (e.g., FC-95) was hindered by an overabundance of interferring compounds.

Integrity of the Standards:

After the initial report[1], it was brought up that FM-3923 and FM-3422 are both the same compound (N-ethyl FOSE alcohol)[3]. The compound used for our FM-3923 standard had given a different retention time, by gas chromatography, than FM-3422. Samples of FM-3923 (a new sample), FM-3923 (the old "standard"), FM-3422, and FM-3925 were sent to Commercial Chemicals Analytical Lab for verification. It was determined that the old FM-3923 standard had been improperly labeled before being sent to us. In reality, the sample was F-6309 (N-ethylperfluorooctanesulfonamide: $C_8F_{17}SO_2NHEt$).

As of 27 August 1979, the new FM-3923, Lot 518, will be used for preparation of standards (identification verified[4]) and the old FM-3923 has been properly labeled as F-6309.

References:

[1]Gagnon, James E., 3M Technical Report Summary "Bioaccumulation of Fluorochemicals in Tennessee River Fish," 22 May 1979.

[2]Hagen, D. F., 3M Technical Report Summary "AR No. 7238 - Determination of Fluorinated Alcohols in Fish Extracts," 23 October 1979.

[3]Personal Communication with A. Mendel.

[4]Winter, L. D., Commercial Chemicals Analytical Lab Request No. 14998, 24 August 1979.

J E Gagnon 2 Jan 80

JEG/cel

6. *Report No. 001 (5/22/79) "Bioaccumulation of Fluorochemicals in Tenn. River Fish" and Report No. 100 (12/28/79) "Fluorochemicals in Tennessee River Fish."*

This pair of papers is quite confusing, largely because of incorrect standards, confused identity of labels and verity of contents, and the difficulty of actual determinations. When these are combined with a lack of clear sampling design in relation to outfall and sampling points, the result add little to our understanding of the problem. These papers make an excellent example of how a little knowledge can be dangerous.

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Form 6747-11-A

TECHNICAL REPORT SUMMARY

CLOSED

NOV 07 1979

Date: October 23, 1979

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

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

Division: CENTRAL RESEARCH LABORATORIES, Analytical and Properties Research Laboratory	Dept. Number: 0502
Project: Environmental Engineering and Pollution Control	Project Number: A000007
Report Title: AR No. 7238 - Determination of Fluorinated Alcohols in Fish Extracts	Report Number: 238
To: J. E. GAGNON - 209-1S	
Author(s): D. F. HAGEN - 201-1S	Employee Number(s): 042608
Notebook Reference:	No. of Pages Including Coversheet: 18 (3)

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.)

Central Research
Analytical Report
Chemical Analysis

CURRENT OBJECTIVE:

Request No. A73154

Requestor - J. E. Gagnon

Project No. 91500600

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.

The microwave sustained helium plasma detector system and capillary column with electron capture detection were utilized to examine fish extracts for fluorocarbon alcohol levels.

Information Liaison Initials

FORM 2643-C PWO

CENTRAL ANALYTICAL LABORATORY

Report No. 7238

Date October 23, 1979

Subject: Determination of Fluorinated Alcohols in Fish Extracts

Requestor: J. E. Cagnon Dept. Name EE&PC Proj. No. 91500600

Request No. A73154 Dated August 8, 1979

Report:

Introduction

The microwave sustained helium plasma detector (MPD-850)-chromatographic systems and capillary column chromatography with electron capture detection were utilized to examine fish extract samples for the presence of fluorocarbon alcohols FM-3923, FM-3925, and FM-3422.

Discussion and Results

The helium plasma detector yields atomic line spectra for the elements present in the chromatographic peak as it elutes from the column. One can therefore monitor specifically for fluorine and sulfur to allow for the detection of specific compounds such as the fluorocarbon alcohols. Detection levels are intermediate between FID and EC detectors. In this type of sample, the lower detection limit is somewhat dictated by the sample matrix. If large non-fluorine containing peaks are present they will overload the plasma activating a "bypass mode" to prevent carbon buildup on the quartz cavity tube. This presents little difficulty if the non-fluorine interference peaks are adequately separated from the fluorine containing peak of interest. The lower level of the fluorocarbon alcohols detectable in these ethyl acetate fish extracts is about 5 nanograms/10µl injection.

Additional sensitivity was obtained by concentrating 100µl of the solution as received to 20µl and injecting 10µl of this concentrate for analysis. Operating conditions for the MPD-850 are listed below.

Column System A - 6', 6% CW-20M-TPA on 80/100 mesh Chrom G. H.P. programmed from 100 to 200°C at 15°C/min. Helium carrier at 25cc/min. with purge rate to MPD of 50 cc/min. Forty percent of the column effluent is split to the FID on the HP-7620 gas chromatograph and 60% is transferred to the MPD-850 plasma cavity via a heated 1/16" capillary line at 180°C. The cavity head temperature is held at 200°C and the plasma is sustained by a 100 watt microwave power supply operating at 2.450 gigahertz. The emission lines used for fluorine and sulfur were 6856.0 and 5453.9 Å respectively. Approximately 0.5 ml/min. of oxygen is used as the scavenger gas to prevent carbon buildup on the quartz plasma reactor tubes.

The above samples were also examined on a capillary column system with electron capture detection in an attempt to lower the sensitivity levels for the compounds of interest. Operating conditions for the capillary system are listed below.

Column System B - 30 meter glass capillary column wall coated with CW-20M. Initial column temperature was 60°C and it was programmed at 10°C/min. to 240°C. Split mode of injection was utilized with 99% of the injected sample (1µl) being vented to the

atmosphere. Column flow was approximately 1 cc He/min. and an auxillary flow of 41 cc/min. of 95-5 Argon-methane was utilized to purge the electron capture detector. This purge flow is added at the exit of the column system on the HP-5840.

System A - Chromatogram 10-10-79-1 illustrates the fluorine and sulfur responses for a 10µl injection of a 10 ppm solution of FM-3923 or $C_8F_{17}SO_2N(CH_3)\ C_2H_4OH$. Note that three fluorine peaks are observed with the major at 6.5 min. The sulfur response lags the fluorine response by 0.5 min. to prevent pen overlap.

Chromatogram 10-10-79-2 results from a 10µl injection of sample 1-M (ethyl acetate extract of a brown bullhead from Minnesota. Note the absence of fluorine containing peaks.

Chromatogram 10-10-79-3A illustrates the results for a 10µl injection of sample 3-A (ethyl acetate extract of a channel catfish above Wheeler Dam). At those points where an overload is shown, the effluent peak which is non-fluorinated is bypassed around the plasma cavity tube. Clear areas do exist however where the fluorocarbon alcohols elute and they appear to be absent.

Chromatogram 10-10-79-4 shows the response obtained for a 10µl injection of the ethyl acetate extract of sample 1-B (bass below Wheeler Dam).

Chromatogram 10-10-79-5 illustrates the response obtained for a 5 fold concentrate of sample 1-B.

Chromatogram 10-10-79-6 shows the response for a 10µl injection of a 5 fold concentrate of sample 3A.

Chromatograms 10-10-79-7 and 10-10-79-8 illustrate the responses obtained for the injection of 1µl of 10 ppm solutions of FM-3923 and FM-3925 respectively. Note the FM-3925 $C_8F_{17}SO_2N\ (C_2H_5)\ C_2H_4OH$ elutes approximately 2 minutes after the n-methyl homolog.

These levels correspond to 10 nanograms injected and I expect one could detect a 5 nanogram level.

Chromatogram 10-10-79-9 illustrates the sample of 1M which has been spiked with known levels of these homologs. In this case 20 ng of each species was added to 100µl of sample 1-A and this was concentrated via evaporation to 20µl. 10µl were then injected for the analysis.

System B - Chromatograms 10-12-79-1, 10-12-79-2, and 10-12-79-3 illustrate the electron capture response for samples 3-A, 1-M, and 1-B respectively. Note the large number of capture sensitive peaks. These are not necessarily halogenated species in that a number of compound classes give a degree of EC reponse. The arrows point out those areas where the alcohol homologs will elute as illustrated in chromatograms 10-12-79-4 and 10-12-79-5.

The capillary column-electron capture results indicate that sample 1-M would have to contain less than 0.05 ppm based on the attenuations for the sample vs. reference solutions. Samples 3-A and 1-B would also contain very little of the FM-3925 or

FM-3422 species. These latter two samples do have a peak at the retention time of FM-3923 major isomer but the isomer distribution is not evident in the sample chromatogram. Lower levels of detection via electron capture would require additional sample cleanup prior to chromatography.

The results obtained by the microwave plasma detector on spiked samples show that these alcohols if present could have been detected from their fluorine content at the 0.1 ppm level in the ethyl acetate extracts. No fluorocarbon peaks were observed in the actual samples.

D. F. Hagen

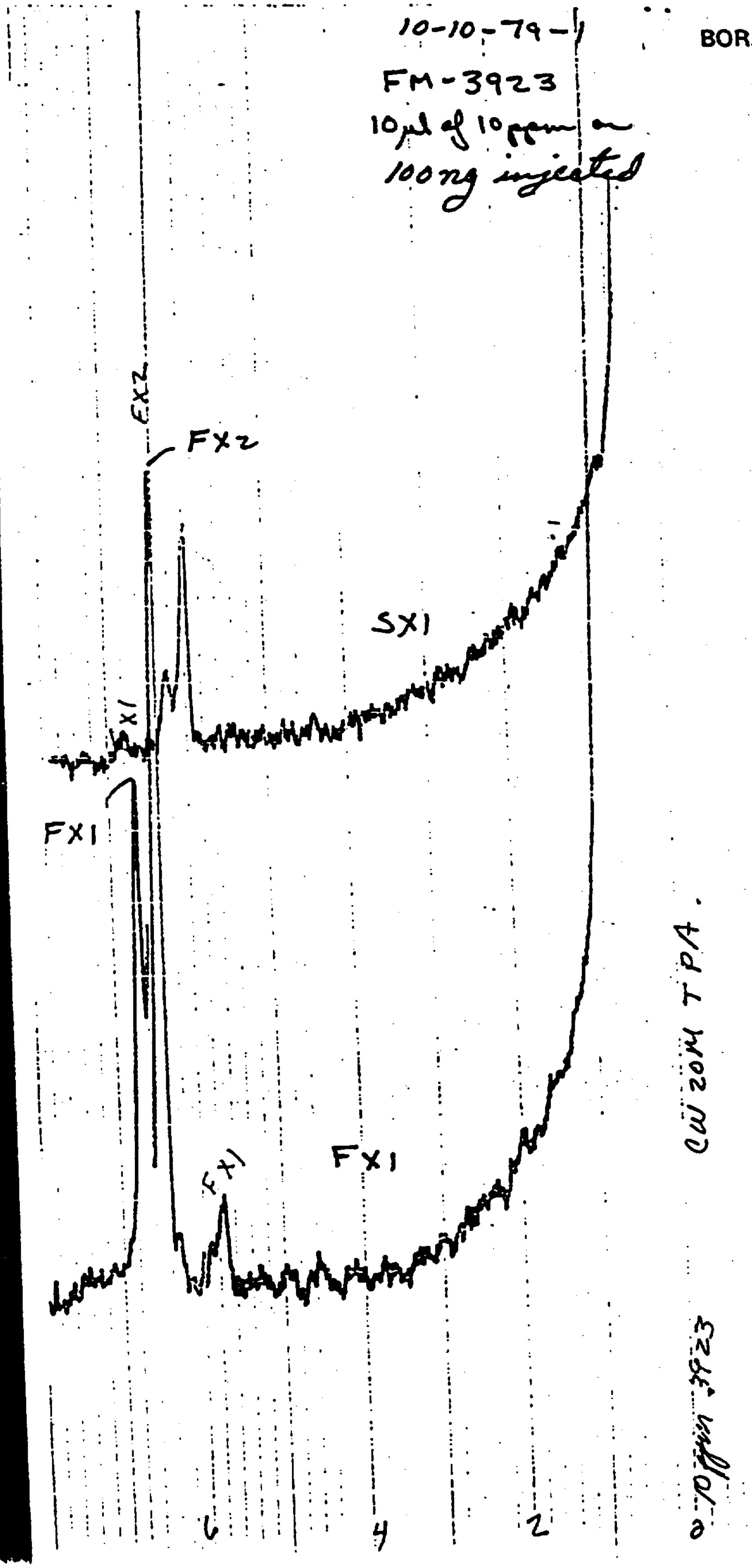
DFH/rs

c: B. W. Nippoldt - 201-1S

FOR :644-O

BORATORIES ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+PC
Project No. 91504500
Date 10/10/79
Chemist Don Hagen



ref.

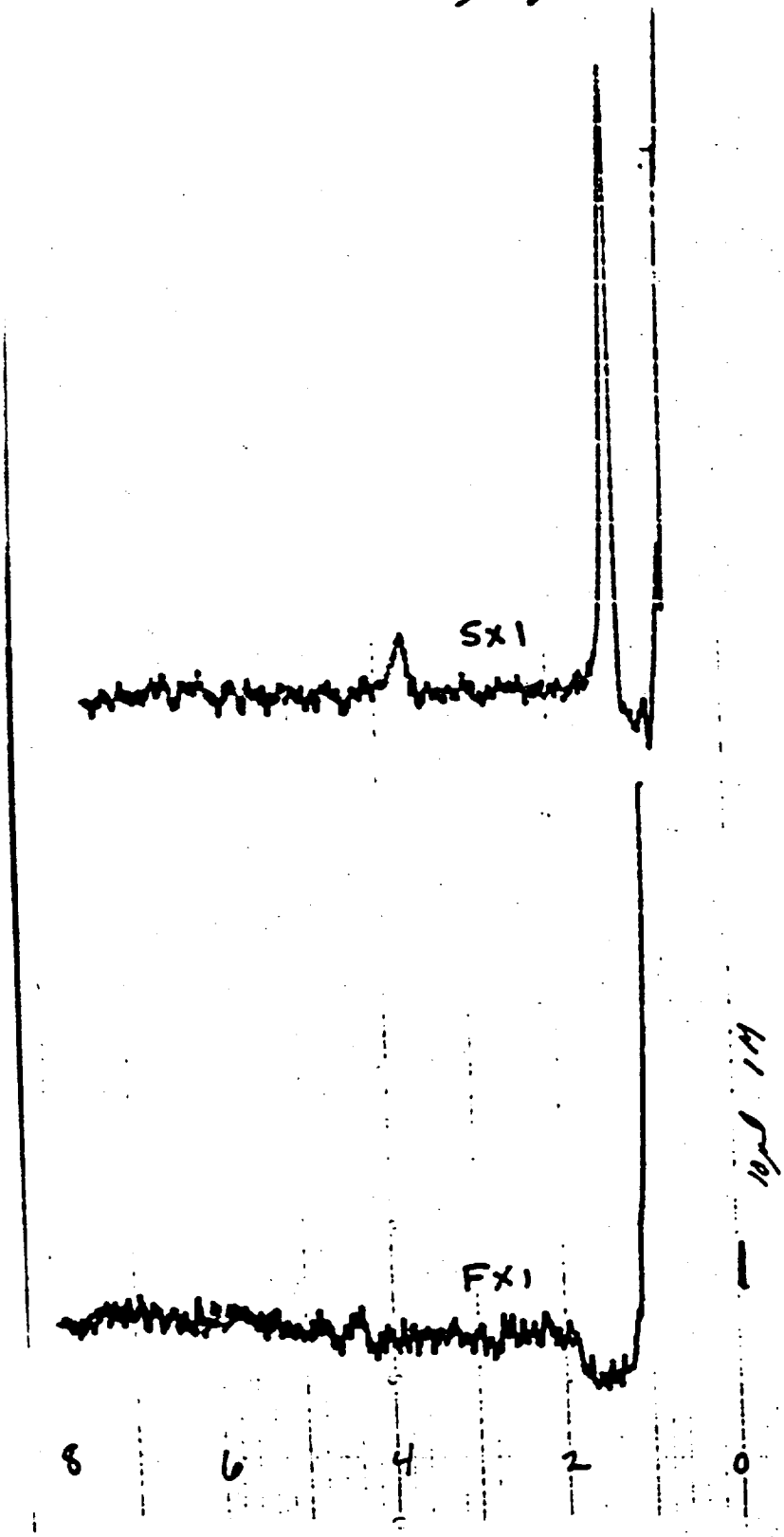
$C_8F_{17}SO_2N(CH_3)C_2H_4OH$

10-10-79-2 LABORATORIES ANALYTICAL RESEARCH

10 µl of 1-M

Request No. A-73154
Div./Dept. EE+PC
Project No. 915045000
Date 10/10/79
Chemist Don Hagen.

1M is ethyl acetate extract of brown bullhead from Minn



FORM 2644-D

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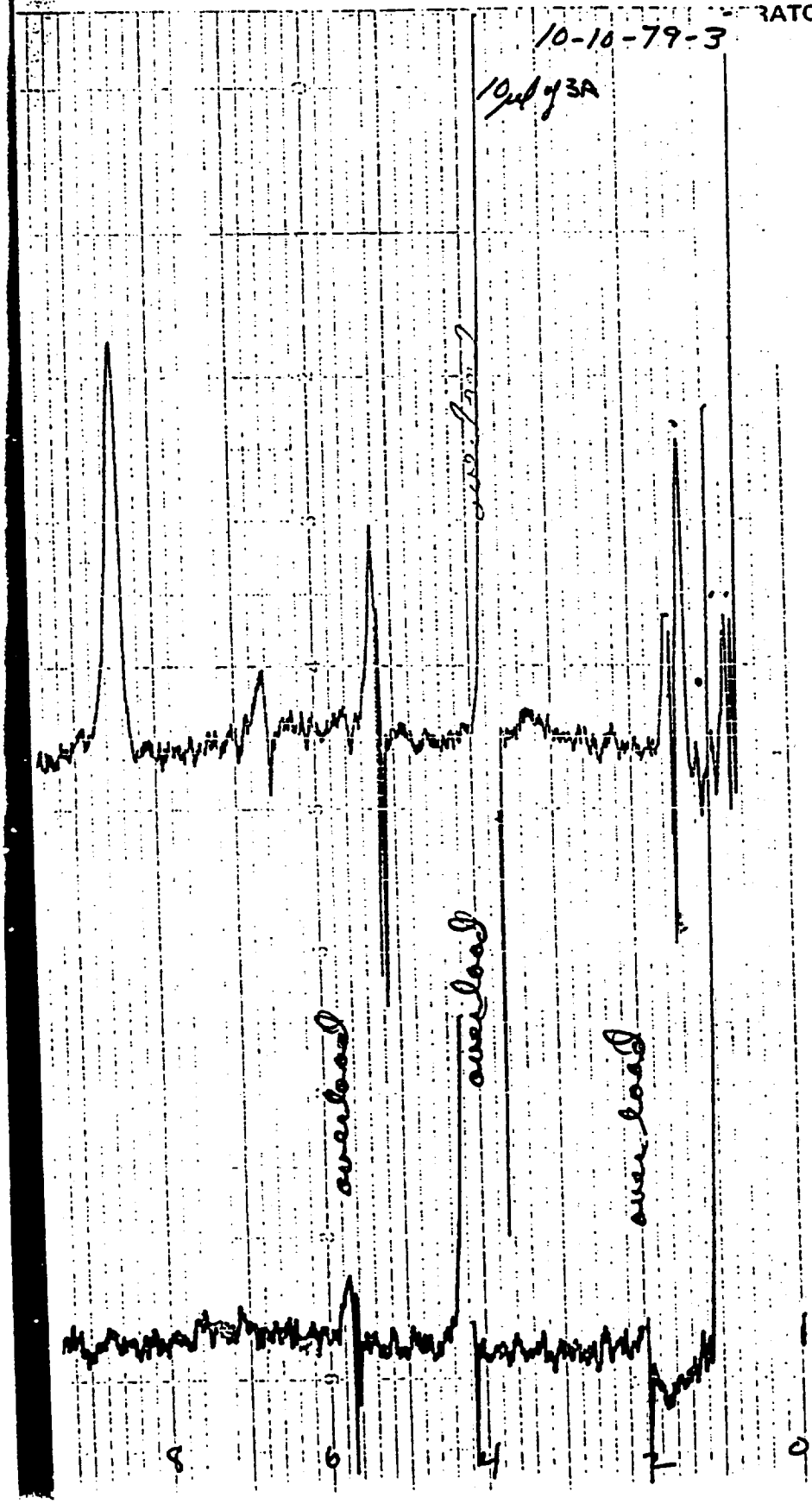
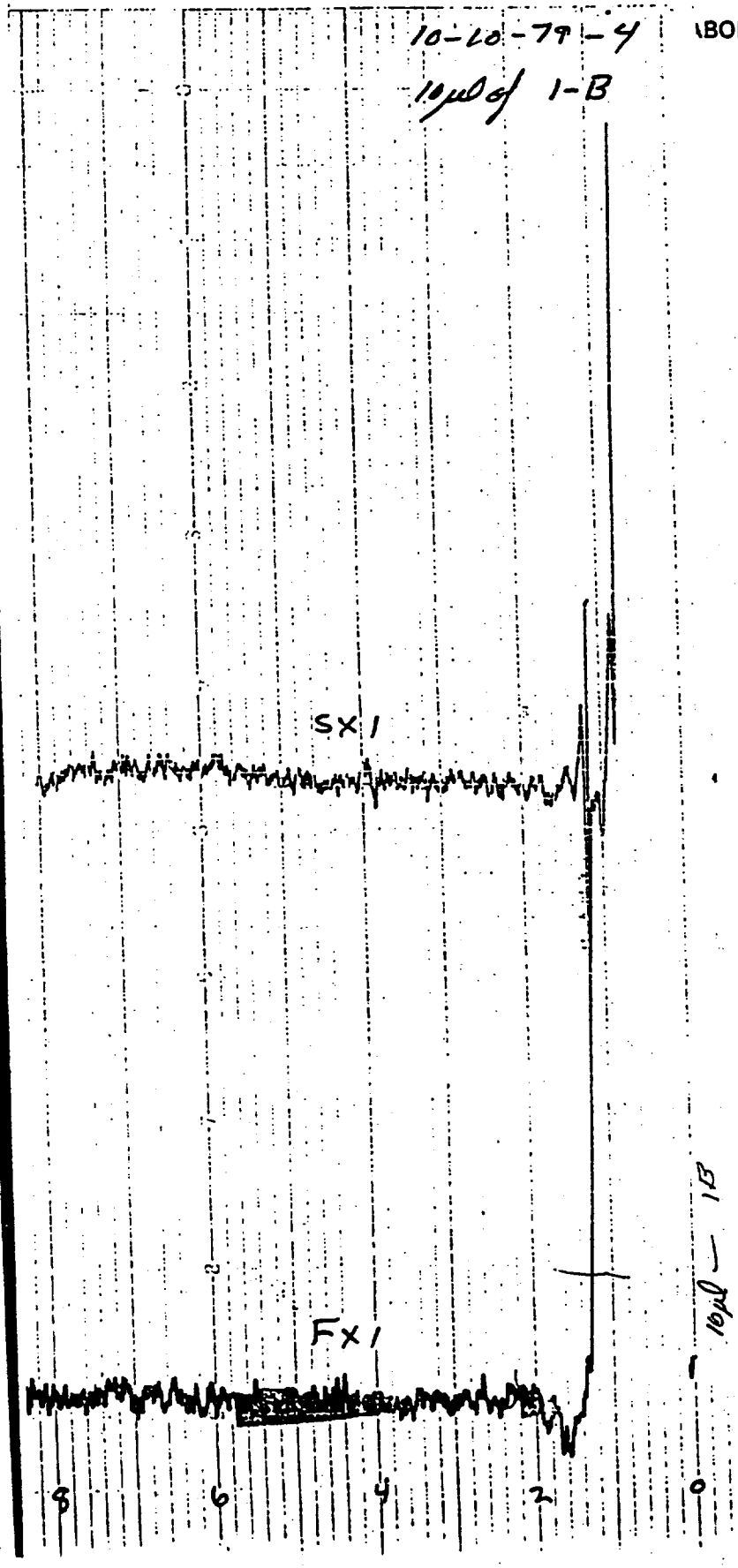
ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+P.C.
Project No. 9150450 0
Date 10/10/79
Chemist Don Hagen.



3A is ethyl acetate extract of channel catfish above Wheeler Dam.

FORM 2644-O

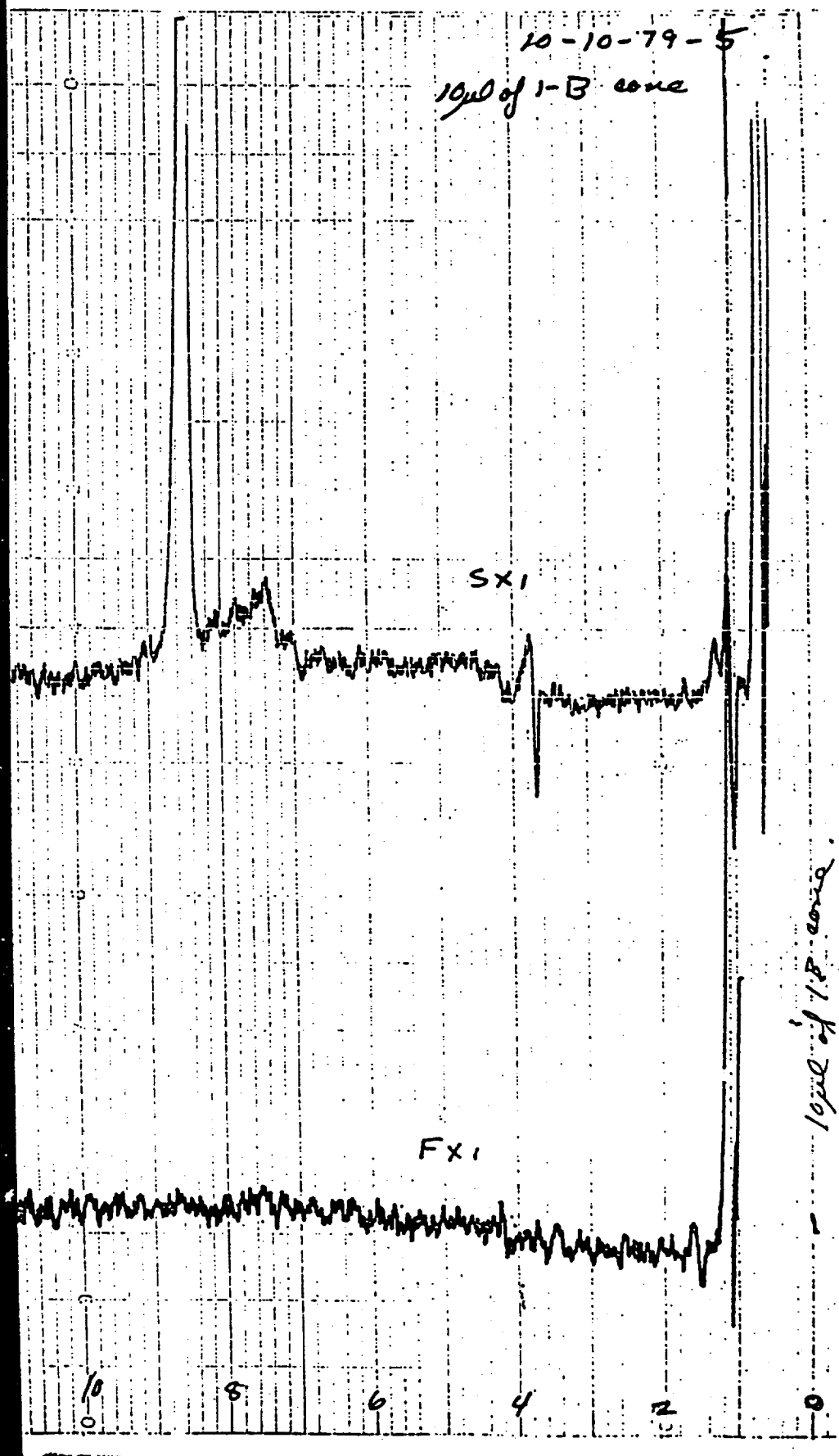


LABORATORIES ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+P.C.
Project No. 91504500
Date 10/10/79
Chemist Don Hagen

1-B is ethyl acetate extract of bass below Wheeler Dam

FORM 2644-D



ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE + PC
Project No. 91504500
Date 10/10/79
Chemist Don Hagemann

200µl of soln of Ethyl nitrate was evaporated to 20µl.

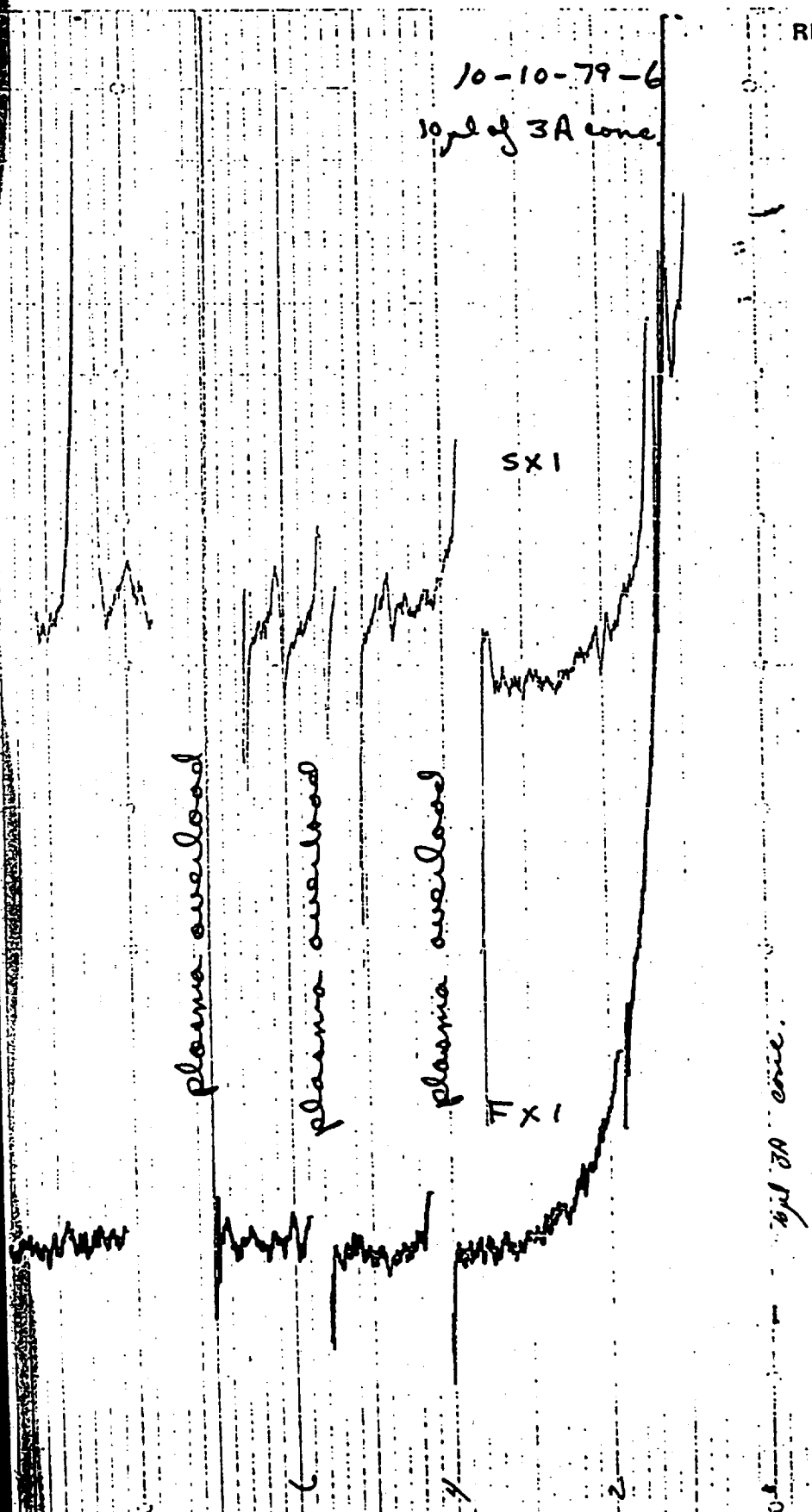
injected 10µl of conc.

FORM 2644-D

RIES ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+PS
Project No. 91504500
Date 10/10/79
Chemist Don Kagan

200µl of ethyl acetate soln was evaporated to 20µl. Injected 10µl of conc.



FORM 2644-D

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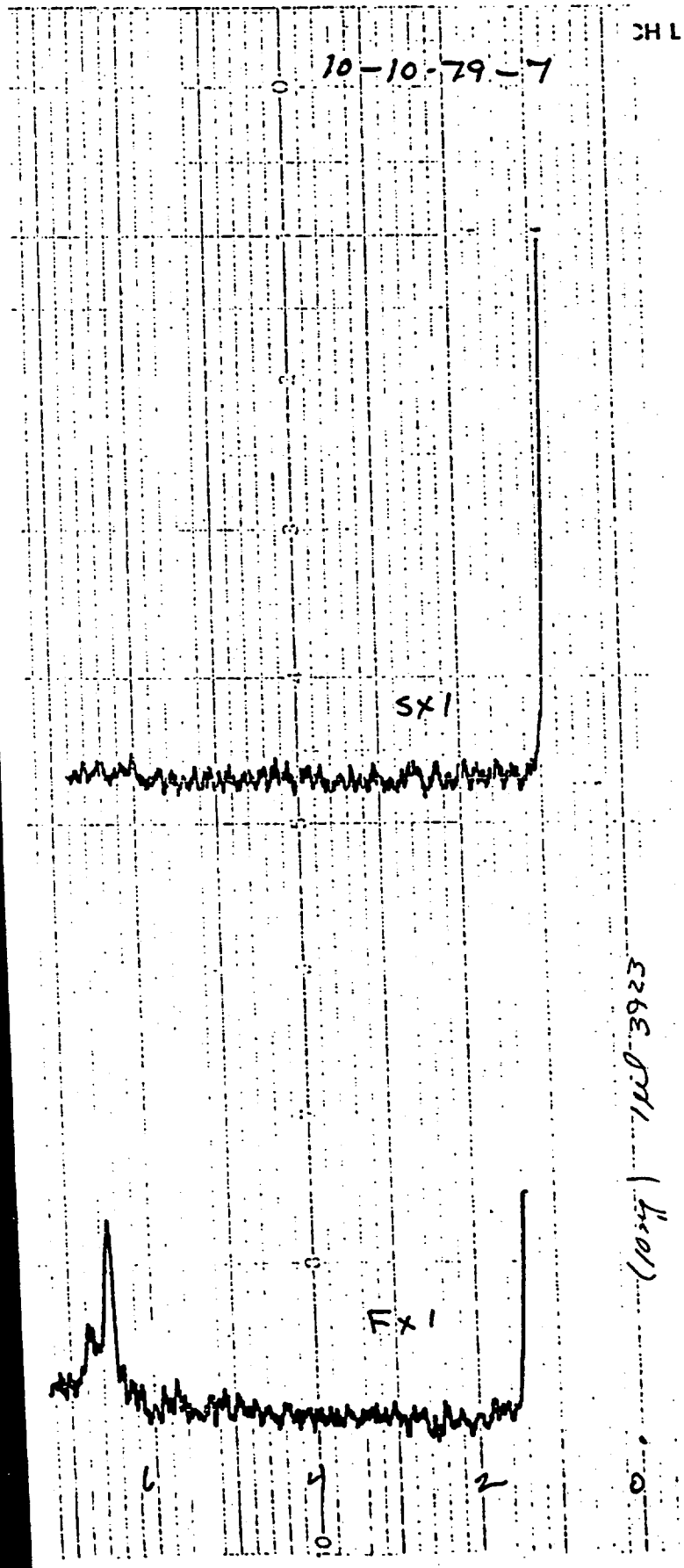
ANALYTICAL RESEARCH

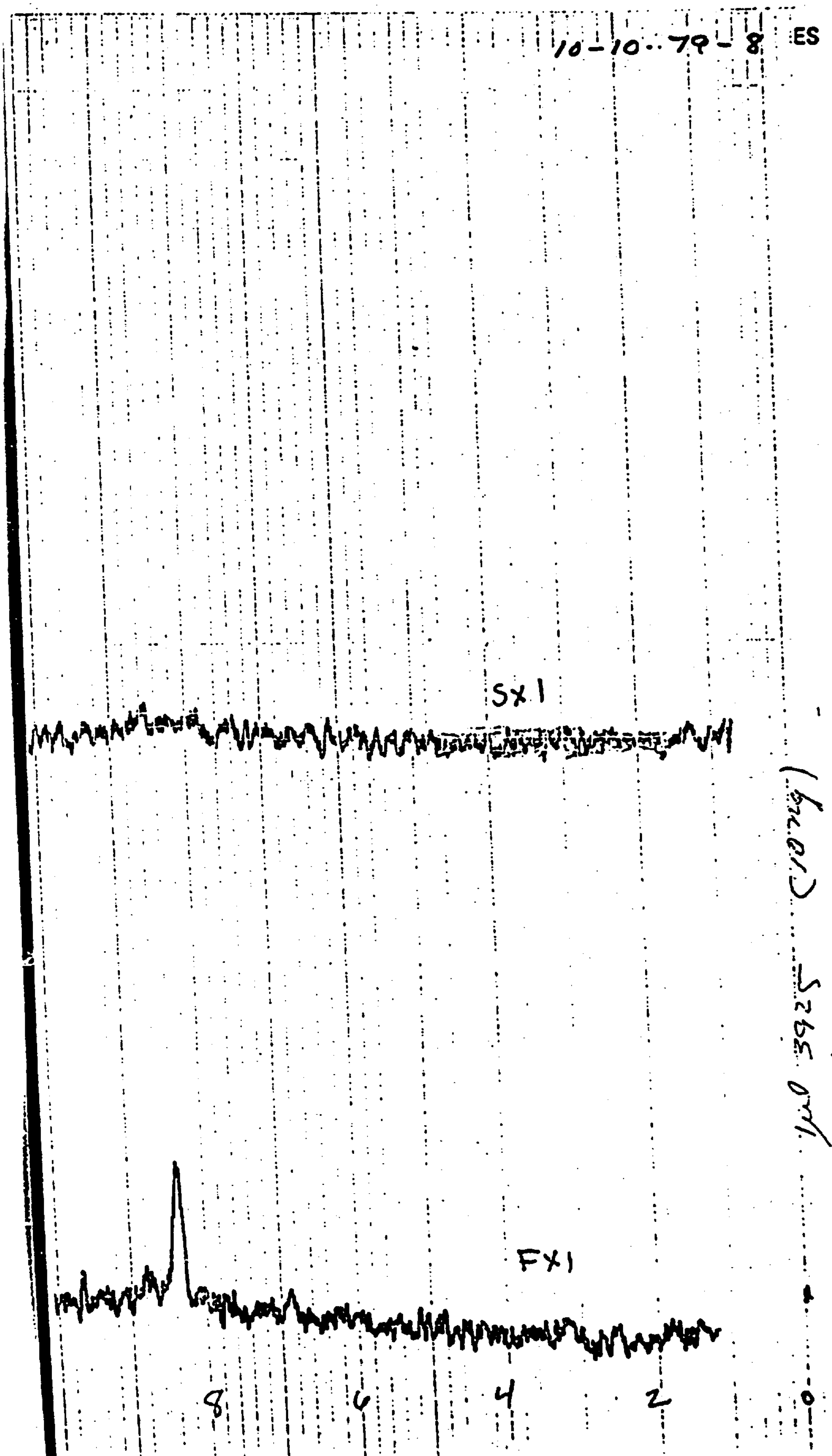
Request No. A-73154
Div./Dept. EE+PC
Project No. 91504500
Date 10/10/79
Chemist Don Hagen.

1 µl of 10 ppm std of FM-3923
on 10 ng injected.

$C_8F_{17}SO_2N(CH_3)C_2H_4OH$



FORM 2644-D



ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+PC
Project No. 91504500
Date 10/10/79
Chemist Don Hagen

1µl of 10ppm std of
FM-3925 or
10ng injected

$C_8F_{17}SO_2N(C_2H_5)(C_2H_4OH)$

FORM 2644-D

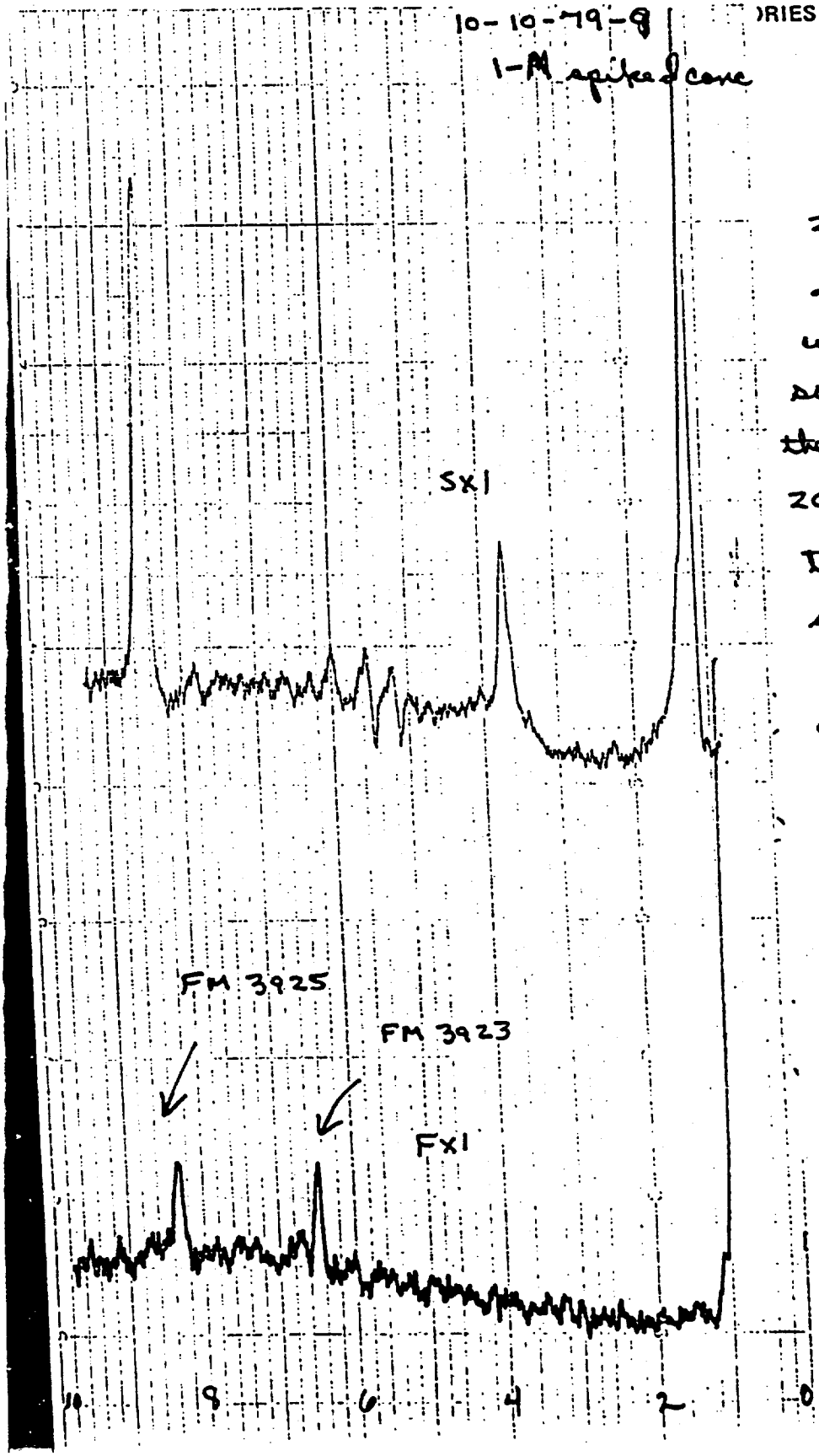
ORIES

ANALYTICAL RESEARCH

Request No. A-73154
Div./Dept. EE+PC
Project No. 9150450 0
Date 10/10/79
Chemist Dan Hagen

10-10-79-9

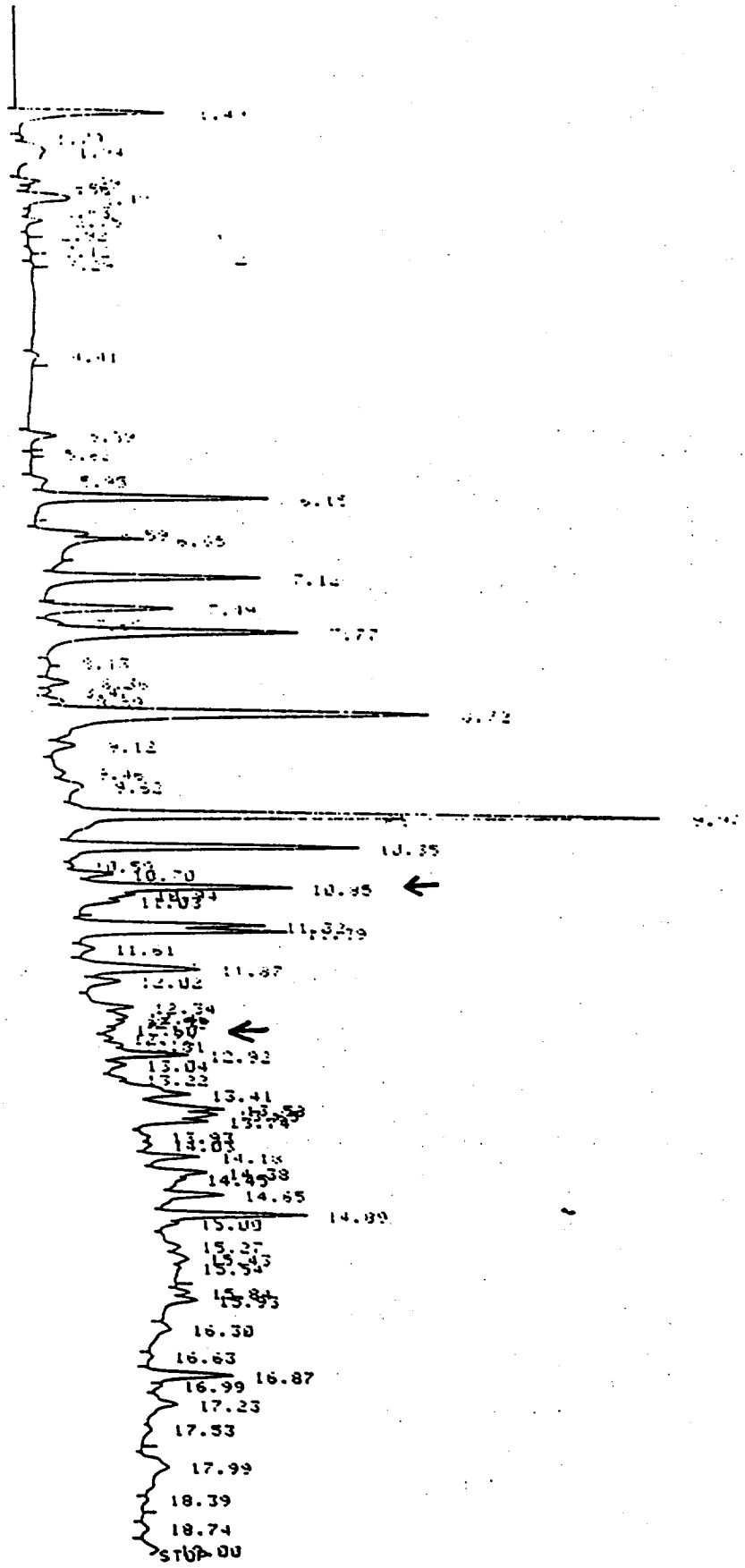
1-M spiked cone



2µl of 10ppm FM-3923 and FM-3925 (20ng) was added to 100µl of sample 1-A. It was then concentrated to 20µl and 10µl was injected. This corresponds to 10 ng injected.

This demonstrates that 0.1 ppm of these alcohol could be detected with peak hts of 7-8 units

Image 3-A
attn 2"



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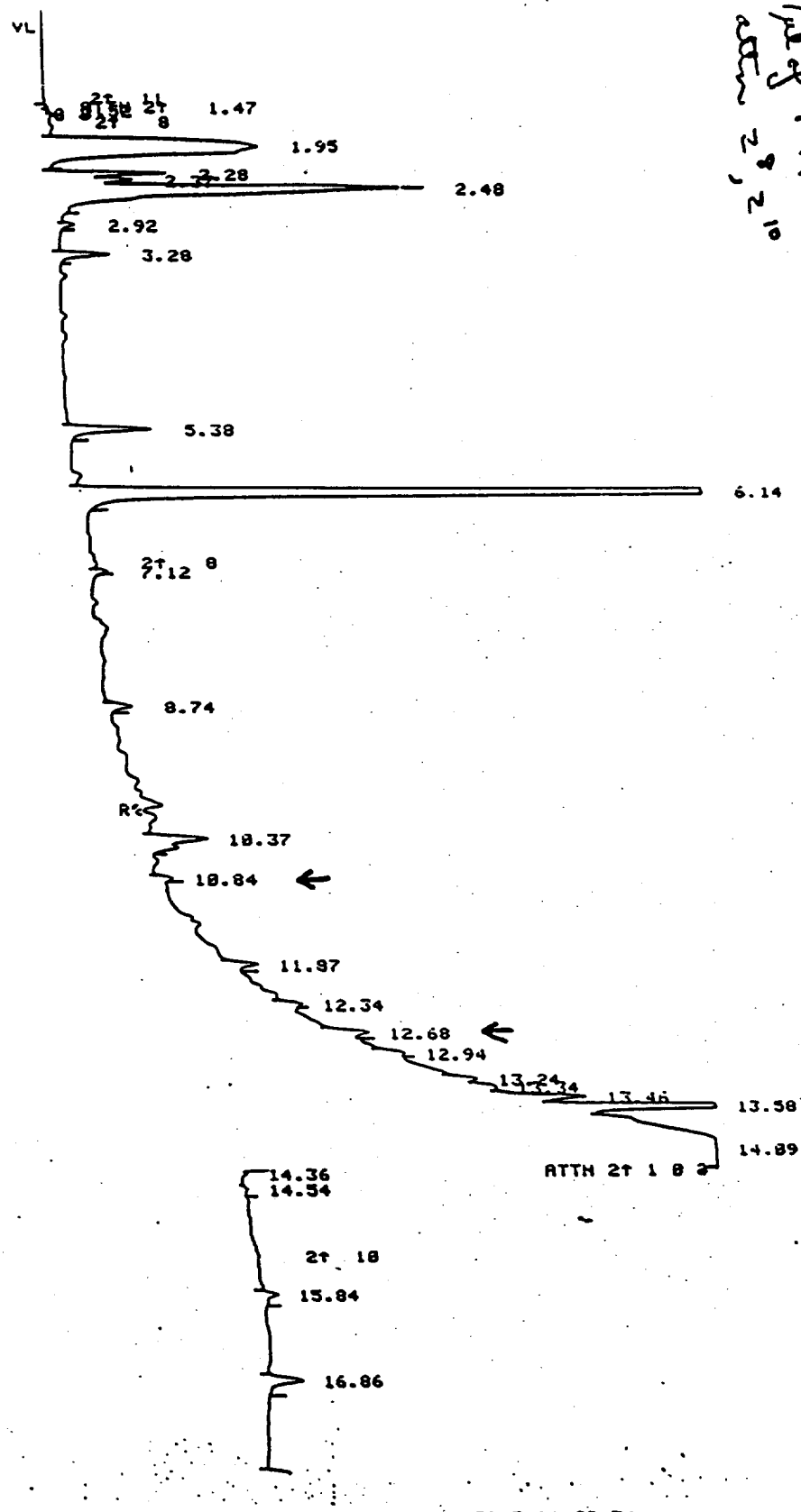
AREA %

RT	AREA	AREA %



HP RUN 8 43 OCT/12/79 TIME 11:02:34
ID:53570-800
AREA %

RT	AREA	AREA %
1.47	2477	0.244
1.52	3808	0.375
1.95	121608	11.977
2.28	16118	1.587
2.37	14138	1.392
2.48	126788	12.486

10-12-79 - 2

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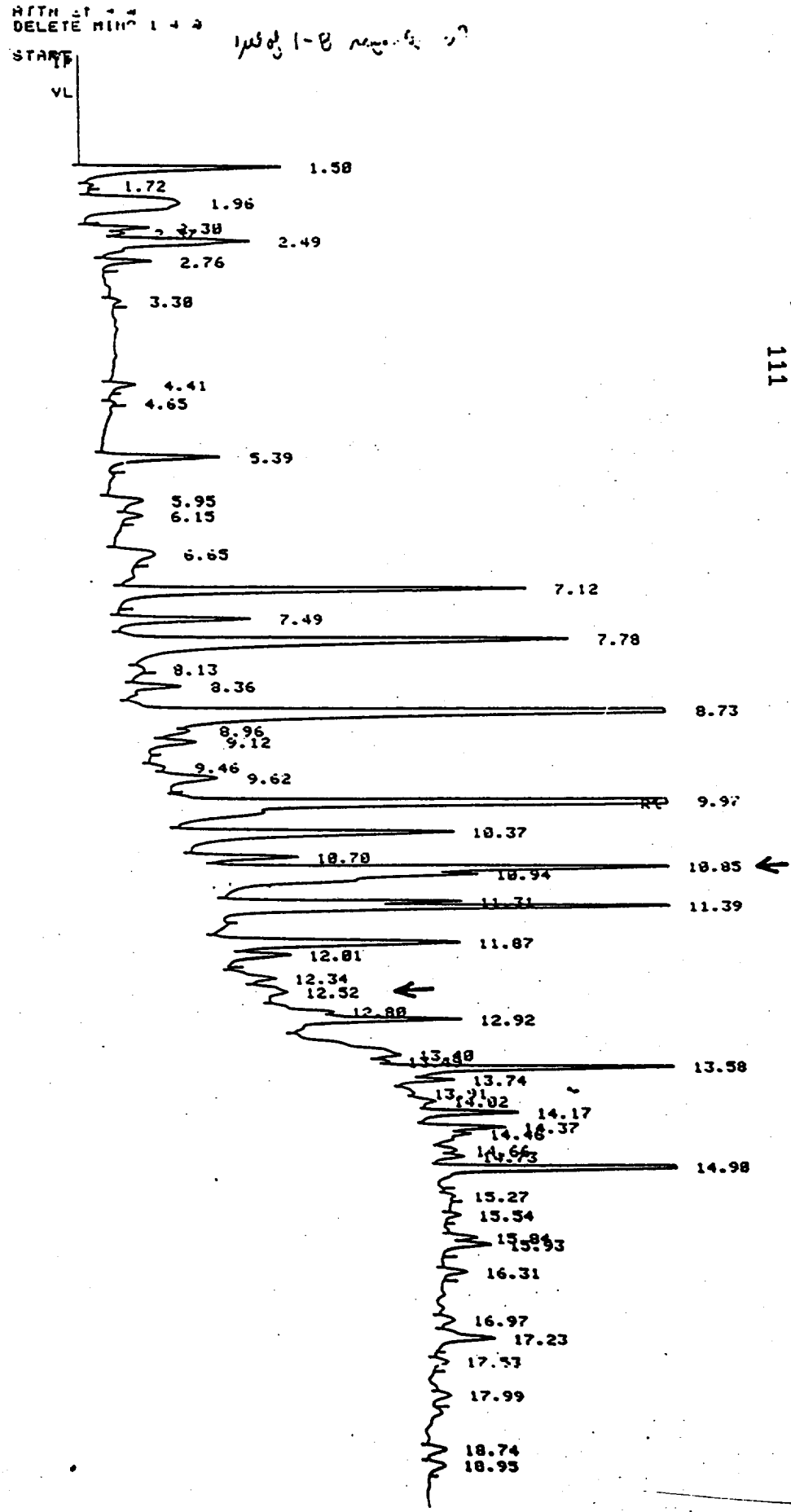
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START
VL
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1.72
1.96
2.38
2.49
2.76
3.38
4.41
4.65
5.39
5.95
6.15
6.65
7.12
7.49
7.78
8.13
8.36
8.73
8.96
9.12
9.46
9.62
9.97
10.37
10.70
10.85
10.94
11.39
11.87
12.01
12.34
12.52
12.80
12.92
13.58
13.74
14.02
14.17
14.37
14.98
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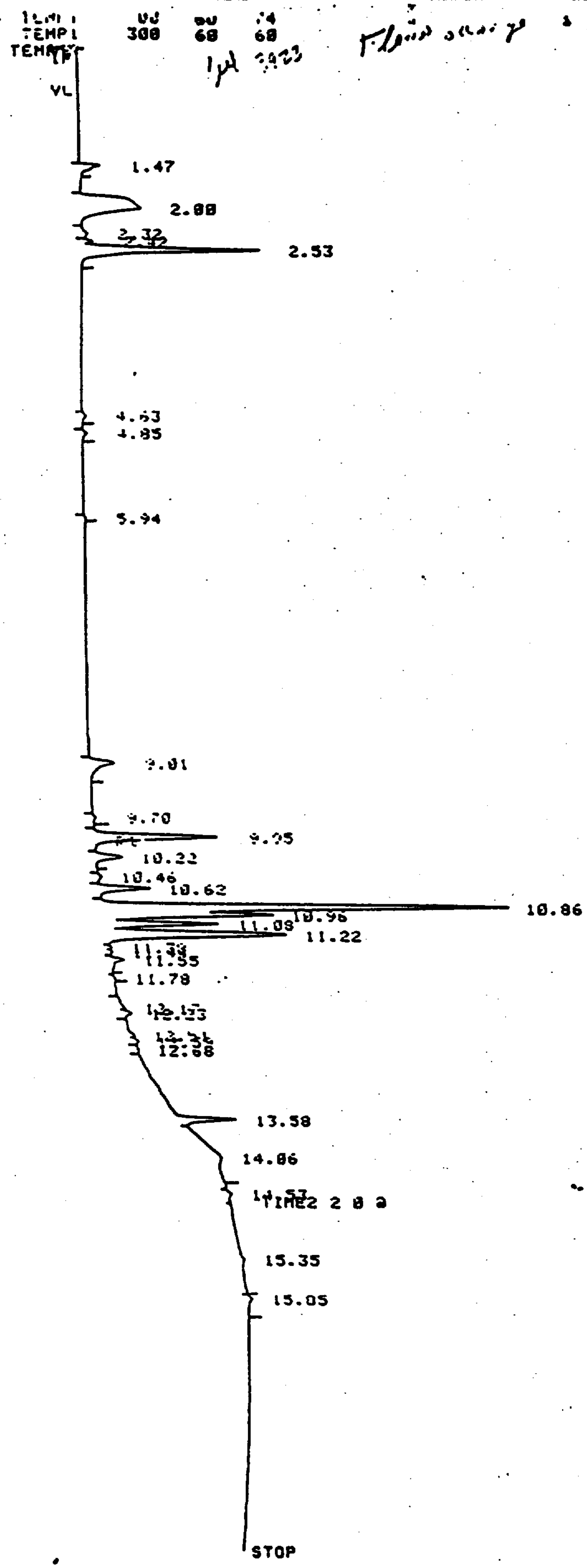
18.74
18.95

111

112



10-12-79-4
1µl FM 3923 reference
atten 2^11

10-12-79-5

1µl FM 3422 reference (10ppm)

attn 2"